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on

Development of a Technique for Contact
Angle Measurements on Irregularly
Shaped Solid Particles

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INTRODUCTION

It has been long known that coal possesses an inherent floatability which depends on its hydrophobic character. This natural hydrophobicity is different for coals of different rank, and the contact angle as a means of evaluation can be used to characterize the floatability of coal. The earlier contact angle measurements were performed with bulk coal samples because methods for contact angle measurements on small, irregularly shaped solid particles have not been available in the past. However, we have recently developed a novel technique for the measurement of contact angles on small particles and we applied this technique to the determination of contact angles on coal particles in Phase I of this contract.

We studied three different coal samples, each of them consists of seven fraction sizes identified by a mesh range. The surface tension, γ_{pv} , and the contact angles, θ , of coal particles were determined by solidification front experiments. This method considers the behaviour of the test particles at the solidification front of solidifying matrix materials such as thymol, biphenyl and naphthalene.

Our approach has two levels:

- 1) The first level consists of the "ranking" of the coal samples in comparison with the surface tension, γ_{LV} , of the organic matrix materials. It is possible to determine the

range of the surface tension of particles, γ_{pv} , by performing a series of engulfing experiments with the matrices of different surface tension, γ_{lv} , since the condition for particle engulfment at arbitrarily small values of the rate of solidification is $\gamma_{pv} < \gamma_{lv}$.

2) The second level of investigations involves the determination of the critical velocity of engulfing, V_c , as a function of particle diameter. V_c can be determined experimentally, and it can be correlated with the free energy of adhesion (ΔF^{adh}), and therefore the various surface tensions and contact angles by dimensional analysis.

In the course of these experiments it became clear that the literature values of some of the physical properties of coal, particularly specific heat and thermal conductivity, were not adequate for the level 2 calculations. The measurements of V_c strongly suggested that there might be a variation of physical properties with particle size. It became therefore highly desirable to assess easily accessible physical quantities, i.e. ash content, moisture content, mineral composition (by means of neutron activation analysis) as these quantities would also have to show variations consistent with those of the surface tension γ_{pv} and the contact angles as inferred from the V_c data. Obviously, such data are also of interest in their own right.

Of the two most crucial quantities needed for the quantitative interpretation of the critical velocities V_c , i.e. the

specific heat of the particles and their thermal conductivity, we adapted Differential Scanning Calorimetry to measure the former. Estimates for the possible ranges of the value of the thermal conductivity of the coal particles were obtained from the interpretation of the V_c data.

Contact angle data for the three coal samples were obtained from freezing front experiments as outlined in the contract application.

We note here that the complexity and the variability of the coal samples, not anticipated by either contractor nor contractee, forced us into the investigation of physical properties on a scope far broader than specified in the contract. In our opinion, most benefits would accrue in the future if the scope of these contracts would be adjusted to allow a more systematic study of the relevant bulk properties of the coal particles in addition to the surface properties.

EXPERIMENTAL RESULTS

I. GENERAL PHYSICAL PROPERTIES

Although we were charged with the examination of the wetting behaviour of the different coal samples, some of the physical properties of coals had to be determined, as explained above.

It was pointed out in our INTERIM REPORT FOR EMR CONTRACT (March 31st, 1980) that using the dimensional analysis for the calculation of surface tension values of coal samples on level 2, the calculated values of γ_{pv} contradicted the values obtained from the "ranking" series (level 1) of engulfing experiments. This contradiction was believed to arise from errors in the values of the physical properties of coal samples. These errors might have arisen by using average bulk values obtained from the literature for specific heat and thermal conductivity.

1. DENSITY, SPECIFIC HEAT AND THERMAL CONDUCTIVITY

The indications were that specific heat and thermal conductivity were different for different particle sizes. Therefore these parameters had to be determined per coal fraction. For all of the experiments two bitumenous (sample No. 1 and No. 2) and one subbitumenous coal (sample No. 3) were provided by EMR. The three coal samples consist of seven fraction sizes each, identified by a mesh range. Table 1 contains the size range in μm and a representative effective

diameter. In cases of coal sample No. 1 and No. 2 the "head sample" was -60 mesh, while the head sample of coal No. 3 was -65 mesh size.

Coal samples No. 1, 2 and 3 were wet screened and oven dried at 105°C before the experiments by EMR Western Research Laboratories (WRL). Seven fractions of coal sample No. 3 were just dry screened and provided for our experiments. Henceforth, the two differently pretreated coal samples No. 3 will be referred to as "coal No. 3 wet" and "coal No. 3 dry".

1.1 DENSITY, ρ [g/cm³]

The density per fraction size was determined experimentally and was provided by EMR-WRL. The density values of the three coal samples are summarized in Table 2. In Figure 1, the density vs. mesh size of the coal fractions is plotted. For the three coal samples, the density shows a minimum in the range of 200-300 mesh, and the density increases in the following order: coal No. 1 < No. 2 < No. 3.

1.2 SPECIFIC HEAT C_p [Cal/(g°K)]

The heat capacity of coal can be measured by standard calorimetric methods at constant pressure (method of mixtures, or by Bunsen's ice calorimeter). Since the heat capacity is measured per unit mass rather than per unit volume, samples of any size or shape may be used [1,2]. Specific heat of a substance is the ratio of its thermal capacity to that of

water at 15°C. Since the specific heat of coal varies with moisture contents, it is usually most convenient to determine the specific heat of dry coal.

The specific heat of coal samples No. 2, No. 3 wet, No. 3 dry for all of the fractions and that of coal No. 1 for one mesh size were determined by Differential Scanning Calorimetry (DSC) using a (Perkin-Elmer Model DSC-2 [3]). Basically, two miniature sample holders are kept at constant temperature by supplying different amounts of electrical power to each sample holder. The differential power input is recorded together with time and temperature signals.

Coal samples of known weight as well as Al_2O_3 crystals (Fisher Sci.) for calibration are enclosed in preweighed aluminum capsules and placed into the sample holders.

The mode of operation was as follows. In a preliminary calibration all controls were adjusted so that over the whole temperature range of 300 to 363°K the power recording remained on scale. The heating and cooling rate was chosen as 5°K/min, the chart speed as 20 mm/min, chart range as 5 mV. Nitrogen gas of 99.99% minimum purity was used for purging the sample holders.

The following three series of measurements were performed: First, the empty reference aluminum capsule was run against another empty capsule of known weight. After optimizing the baseline linearity and calibrating the instrument for temperature, a weighed and encapsulated Al_2O_3 standard was placed in

the sample holder and was run for calibration. Then the coal sample (weighed and encapsulated) was run maintaining all prevailing experimental conditions.

Small differences in sample pan weights can be corrected for by using the following equation:

$$D = \frac{\Delta W \times C_{p_{Al}} \times S}{R}$$

where D ordinate displacement [mm]

ΔW difference in pan weights [milligrams]

C_p specific heat of pan material (aluminum) [cal/(g°K)]

S scan rate [degrees/second]

R setting of RANGE control [m cal/sec.inch]

(e.g. the setting the RANGE control in m cal/sec

(full scale) divided by chart span in inches).

The calculated ordinate displacement was added to the displacement of the material run in the lighter pan.

The specific heats of the coal samples can be obtained after the calibration with Al_2O_3 by applying the formula:

$$C_{p_{COAL}} = \frac{W_{Al_2O_3}}{W_{COAL}} \times \frac{D_{COAL}}{D_{Al_2O_3}} \times C_{p_{Al_2O_3}}$$

where

$C_{p_{Al_2O_3}}$ specific heat of Al_2O_3 [cal/(g°K)]

$W_{Al_2O_3}$ weight of Al_2O_3 [milligrams]

W_{COAL} weight of coal sample [milligrams]

$D_{Al_2O_3}$ ordinate displacement of Al_2O_3 , [mm]

D_{COAL} ordinate displacement of coal [mm].

The Al_2O_3 specific heat data used for calibration were obtained from the work of GINNINGS and FURUKAWA [4]. Specific heat values were calculated at 10°K intervals in the temperature range from 300 to 360°K for the coal samples and are summarized for coal No. 1, No. 2, No. 3 wet and No. 3 dry in Tables 3, 4, 5 and 6, respectively.

In Figures 2, 3 and 4 the specific heat values are plotted as a function of fraction mesh size for coal No. 2, No. 3 wet and No. 3 dry, respectively.

The C_p value of coal No. 2 does not vary strongly with particle size. Only a slight increase occurs with increasing mesh size (decreasing particle size). There is a difference between coal No. 3 wet and coal No. 3 dry. The specific heat of the wet sample changes similarly as that of coal No. 2, but the C_p values of the dry sample vary in an irregular fashion. The specific heat vs. temperature for coal No. 1, No. 2, No. 3 wet and No. 3 dry is plotted in Figures 5, 6, 7 and 8, respectively. The two bituminous coal samples (No. 1 and No. 2) show a small increase in specific heat with increasing temperature. The C_p values of coal No. 3 wet, and especially No. 3 dry increase very rapidly with increasing temperature. In Figure 9 the specific heat values vs. temperatures are plotted for the 60-100 mesh fractions of all the coal samples investigated. The different behaviour of the bituminous and subbituminous coal samples

is very noticeable. In Figure 10, the reproducibility of the C_p determination is demonstrated for two fractions (150-200 and 325-400 mesh) of coal sample No. 3 dry.

The large increase of C_p values with increasing temperature might be caused by the higher moisture content and mineral contamination of coal sample No. 3.

1.3 THERMAL CONDUCTIVITY [cal/(sec.cm°K)]

1) The thermal conductivity of coal is strongly dependent on its moisture content, porosity (1,5).

In our INTERIM REPORT it was pointed out that the thermal conductivity value (k) used initially for the calculations, was a bulk value obtained from the literature. We suspected that the relevance of this value may be questionable and that there might be a dependence of thermal conductivity on particle size. The different percentage of ash, moisture, mineral and carbon content will affect the thermal conductivity of the particle and it is conceivable that the actual thermal conductivity for the various fractions is significantly smaller than the bulk value.

At the present time there is no suitable technique to measure the actual thermal conductivity of the different fractions. For coal sample No. 2 an approximate value of k was obtained as follows: The level 1 engulfing experiments yield for each sample a range of possible γ_{pv} values. From the level 2 engulfing experiments it is then possible to impose this range as a boundary condition, and, all other parameters being known, to determine a range of possible k

values for each of the matrix materials considered. For coal sample No. 2 an average thermal conductivity value was estimated consistent with these ranges. This average value is 2.9×10^{-5} [cal/(cm.sec.°K)]. But for coal No. 3 wet and coal No. 3 dry, the specific heat values are not yet sufficiently definite to allow such an interpretation.

2. AUXILIARY PHYSICAL PROPERTIES

As explained in the introduction, already early stages of this work showed considerable variability of the properties even within each of the three types of coal. It thus became desirable to consider other properties and parameters of the coal samples as well. We therefore discuss, below, moisture content, ash content, surface area and chemical analysis by Neutron Activation Analysis.

2.1 MOISTURE CONTENT [%]

According to the information given by EMR-WRL, after crushing the three coal samples were wet screened and oven dried at 105°C. Coal sample No. 3 was also dry screened.

The moisture content of the fractions was determined in our laboratory by measuring the loss in weight by heating at a temperature slightly higher than the boiling point of water. Coal powder (0.2 - 0.5 g) in weighing bottles was oven dried at 105°C until the weight of the sample remained constant (approx. 2 hrs.). After cooling in a desiccator, the loss of weight was determined with analytical accuracy.

The moisture content of the fractions of all coal samples are given in Table 7 and plotted in Figure 11. The bitumenous coals (No. 1 and No. 2) have lower moisture content than the

subbituminous coal No. 3 even after the same pretreatment. The dry screened coal No. 3 sample has a high moisture content (appr. 10%), which is characteristic of the subbituminous coal. It slightly decreases with decreasing particle size.

2.2 ASH CONTENT [%]

The ash content of the fractions of the coal samples is summarized in Table 8. The data of ash content were obtained from EMR Western Research Laboratories, Edmonton. In Figure 12, the percentage of ash content vs. mesh size of the fractions is plotted. For the three wet screened samples, the ash content shows a minimum in the range of 200-400 mesh. The ash content of the dry screened No. 3 sample increases with increasing mesh size (decreasing particle size).

2.3 SURFACE AREA [m^2/g]

The surface area of the coal samples is given in Table 9. The experimental data were provided by EMR-WRL. This determination was performed only with the wet screened coal samples. Surface area vs. mesh size of the coal fractions is plotted in Figure 13. The difference in surface area between bituminous and subbituminous coals is considerable. The subbituminous sample No. 3 has more than ten times higher values. The surface area shows the highest value for the 400 mesh fractions, as expected.

2.4 NEUTRON ACTIVATION ANALYSIS (NAA) OF COAL

The mineral composition of the coal samples was determined by means of neutron activation analysis (NAA) using the University of Toronto's SLOWPOKE reactor.

This technique is based on the measurement of the amount and energy of γ -rays emitted by the radioactive isotopes produced in the sample by irradiation with thermal neutrons. The sample and appropriate standards of the elements of interest are irradiated for a suitable time period in the neutron flux. After irradiation a gamma count energy spectrum is obtained by counting the sample with a scintillation counter. Quantitative analysis is obtained by comparing the characteristic counts and energies of the unknown with the number determined by reference standards. This analysis was performed at 5 KW flux for 20 minutes/mg. The coal standard reference was SRM 1632 from the U.S. National Bureau of Standards, Washington D.C.

The results of neutron activation analysis are summarized for coals No. 1 and No. 2 in Table 10 and for coal No. 3 wet and dry samples in Table 11, respectively. The percentage or ppm values of the elements are plotted vs. mesh size of the fractions for all coal samples in Figures 14-26. (The values of "head sample" (-60, -65 mesh) are not included because this fraction, due its procurement, is not characteristic for the role of particle size of the coal sample).

Comparing the physical parameters of the three coal samples, it was found that the density, ash and moisture contents, specific heat and surface area increase as follows: Coal No. 1 < No. 2 < No. 3. The dry screened samples of coal No. 3 have higher values of the above parameter than the wet screened and oven dried sample.

The same order is found in the contents of U, Dy, Al, Mg, Ca, Mn, Na and Ti (Figures 14-21). The reverse order is found (sample No. 3 < No. 2 < No. 1) in Cl, V contents (Figures 22, 23). Ba and Sr content does not show any regularity (Figures 24, 25).

There is no significant difference in the concentrations of U, Dy, Ti, V and Cl between the wet and dry screened No. 3 samples (Figures 14, 15, 21, 22, 23, respectively). But the concentration of Al, Mg, Br and especially that of Na (Figures 16, 18, 26 and 20, respectively) is higher in the dry screened samples. The most likely explanation of these differences is that these elements often form water soluble compounds which are probably dissolved and washed out during the wet screening process.

It is worth mentioning that coal sample No. 3 has noticeably higher mineral contamination than the standard and average values of mineral elements in coal samples. The uranium and dysprosium concentrations are 3 to 6 times higher in coal No. 3 than in the average coals.

II. PARTICLE ENGULFING STUDIES

The surface tension, γ_{pv} , and contact angle, θ , of small coal particles were determined by solidification front experiments. This method considers the behaviour of the test particles typically in the range of 20-250 μm at the test solidification front of solidifying matrix materials such as pinacol, thymol, biphenyl, naphthalene, salol and 2-phenylphenol.

Particles may either be pushed along by the solidification front or may be engulfed. The driving forces for particle pushing are provided by the interfacial free energies (work done against the interface), whereas the main retarding force appears to be hydrodynamic drag. As the rate of solidification increases the viscous drag opposing the particle motion will increase and at a certain rate, called critical velocity, V_c , the two forces become equal and engulfing occurs. The various particle and matrix (melt) properties that appear in the expressions for the driving and retarding forces can be related by the method of dimensional analysis. V_c can be determined experimentally and correlated with the free energy of adhesion (ΔF^{adh}), the various surface tensions and contact angles.

It was pointed out in our INTERIM REPORT FOR EMR CONTRACT (March 31st, 1980) that two equations resulting from the dimensional analysis were used. Appendices 1, 2, and 3 of the

Interim Report provide in detail the theoretical background, the dimensional analysis and the experimental technique for determining contact angles on small particles. A current dimensional analysis of those experimental results has produced a single equation valid for all particle sizes.

The free energy of adhesion is expressed by

$$\Delta F^{\text{adh}} = 0.141 \left[\frac{\rho_L^{0.6854} T^{0.3995}}{\mu^{0.0849}} \right] \left[\frac{k_P^{0.6005}}{(\rho_P C_P)^{0.2009}} \right] D^{0.4844} V_c^{0.6854} \quad (1)$$

ΔF^{adh} = free energy of adhesion [ergs/cm²]

ρ_L = density of matrix material [g/cm³]

μ = viscosity of matrix material [Poise]

ρ_P = density of particle [g/cm³]

c_P = specific heat of particle [cal/(g°K)]

k_P = thermal conductivity of particle [Cal/(sec.cm°K)]

T_{MP} = melting point of matrix material [°K]

D = diameter of particle [μ m]

V_c = critical velocity of particle engulfing [μ m/sec].

All the physical thermodynamic parameters used for numerical calculations are given in Table 12 for the matrix materials and in Tables 2, 3, 4, 5 and 6, for the coal samples No. 1, No. 2 and No. 3, respectively.

The introduction has discussed the two levels of our approach.

1. LEVEL 1: "RANKING" MEASUREMENTS

The first step in this investigation involved the "ranking" of the three coal samples in comparison with the surface tension,

γ_{LV} , of the organic matrix materials.

This preliminary series of engulfing experiments showed that the hydrophilicity of the coal samples increases in the following order: coal No. 1 < coal No. 2 < coal No. 3.

Coal sample No. 1 was engulfed by thymol, biphenyl, naphthalene, salol and 2-phenylphenol. There exists some doubt concerning the purity of the pinacol used. Therefore the engulfing experiment with pinacol was discounted. The conclusions regarding γ_{PV} and θ for coal sample No. 1 are indicated in Table 13. The low surface tension and the high contact angle values are in good agreement with the bitumenous character of the coal.

For coal sample No. 2, the extensive experiments of the first level 1 approach has shown that all fraction sizes were pushed by thymol, biphenyl, naphthalene and salol, and were engulfed by 2-phenylphenol. The conclusion regarding γ_{PV} and θ for coal sample No. 2 are indicated in Table 14.

This preliminary "ranking" of coal sample No. 2 has defined limits for the surface tension, γ_{PV} , thus providing an experimental base for our second level of investigation.

For coal sample 3 (wet as well as dry) the engulfing experiments showed that all fraction sizes were pushed by thymol, biphenyl, naphthalene, salol and 2-phenylphenol. The conclusions regarding γ_{PV} and θ for coal sample No. 3 are indicated in Tables 15 and 16.

2. LEVEL 2: CRITICAL VELOCITY MEASUREMENTS

The second part of the investigation involved the determination of the critical velocity of engulfment as a function of particle diameter for the matrix materials thymol, biphenyl and naphthalene.

For coal sample No. 2 this work has been completed for thymol, biphenyl and naphthalene. Five fraction sizes were used i.e. fractions 2 to 6 inclusive (see Table 1). The plots of critical velocity, V_c , vs. particle diameter, D , for thymol, biphenyl and naphthalene are shown in Figures 27, 28 and 29, respectively.

For coal sample No. 3 (wet and dry) experiments with thymol using fractions 2 to 6 inclusive and with biphenyl using fractions 3 and 6 were performed. The plots of critical velocity, V_c , vs. particle diameter, D , for thymol and biphenyl are shown in Figures 30, 31, 32 and 33.

The analyses in this second level of investigation considers only the particle sizes in the range 50-270 μm because the critical velocity vs. diameter plots are determined only in this range.

2.1 COAL SAMPLE NO. 2

An initial calculation of the surface tension, γ_{pv} , for a given particle diameter was done and compared with the experimentally determined surface tension limits in Table 14. Using the critical velocity, V_c , corresponding to diameters of 50 μm

and 270 μm from the thymol, biphenyl and naphthalene plots (Figures 27, 28 and 29) plus the physical properties listed in Tables 2, 3, 4, 5 and 6 in conjunction with the literature bulk value of thermal conductivity $\left[7.10^{-4} \left[\frac{\text{cal}}{\text{sec.cm}^{\circ}\text{K}}\right]\right]$ the surface tension, γ_{pv} , for each diameter (50 μm and 270 μm) was calculated. The calculated surface tensions are given in Table 17.

It is evident that the surface tension, γ_{pv} , obtained from equation (1) contradicts the values determined from the level 1 engulfing experiments. Nevertheless there exists good agreement between the thymol, biphenyl and naphthalene systems within experimental error.

Therefore, as explained in Part I of this report, all the physical properties (except thermal conductivity) of coal samples No. 1, 2 and 3 were determined experimentally. It is evident that the density and specific heat are complicated functions of particle size, temperature, mineral composition, etc. Therefore it is reasonable to suppose that the thermal conductivity will be also a complicated function of these parameters, and, as discussed in Part I, may have a value one order of magnitude less than the literature bulk value.

Another important thermodynamic parameter necessary in this analysis is the temperature coefficient of surface tension, $\frac{d\gamma_{\text{pv}}}{dT}$. The "ranking" results and the critical velocity, V_c , vs. particle diameter, D , plots are valid only at the melting point of the matrix material used. In order to interrelate all these results the temperature coefficient of surface tension is required. Again it is reasonable to suppose that the temperature

coefficient of surface tension will be different for different particle sizes.

There remain three unknowns: the thermal conductivity, the temperature coefficient of surface tension and the surface tension, as a function of particle size.

The surface tension range (Table 14) determined by the "ranking" series of engulfing experiments provides limiting values of γ_{py} . We have available plots of critical velocity as a function of particle diameter for three systems: thymol, biphenyl and naphthalene (Figures 27, 28 and 29, respectively). The remaining analysis is analogous to the following mathematical problem: three equations in three unknown variables plus boundary conditions. The solution is determined by solving the equations simultaneously. By judiciously choosing ϵ value for the temperature coefficient of surface tension, $\frac{d\gamma_{py}}{dT}$, and by varying one or both of the boundary conditions it is possible to calculate a permissible thermal conductivity (k_2) range for each of the three systems. The actual surface tension, γ_{py} , of a coal particle must be independent, within experimental error, of the matrix material used. The three systems, thymol, biphenyl and naphthalene must converge upon the "true" surface tension value consistent with the "ranking" limits of surface tension. The calculated permissible thermal conductivity value must be admissible for the three systems. Therefore one can estimate an average thermal conductivity that best conforms to these three k_2 ranges. For this "optimization" process a particle of 50 μm is assumed to correspond to the

lower boundary condition and a particle of 270 μm is assumed to correspond to the higher boundary condition. The outcome of this optimization is as follows:

- the lower boundary condition becomes (see Table 14)

$$\gamma_{PV} > 37.50[\text{ergs}/\text{cm}^2] \text{ at } 43^\circ\text{C}$$

- the upper boundary condition remains (see Table 14)

$$\gamma_{PV} < 38.70[\text{ergs}/\text{cm}^2] \text{ at } 59^\circ\text{C}$$

- the average temperature coefficient of surface tension

$$\frac{d\gamma_{PV}}{dT} = -0.065[\text{ergs}/(\text{cm}^2\text{K})]$$

- Table 18 presents the thermal conductivity k_2 ranges for thymol, biphenyl and naphthalene

- the estimated average thermal conductivity k_2 is

$$k_2 = 2.9 \times 10^{-5}[\text{cal}/(\text{cm}\cdot\text{sec}\cdot^\circ\text{K})] .$$

It is evident that, strictly speaking, an average thermal conductivity value and an average temperature coefficient of surface tension value are at odds with the particle size dependence of the density, the specific heat, the ash content, the moisture content and the mineral composition. But for practical purposes these are useful estimates.

All the parameters in equation (1) are known now. Using the experimentally determined critical velocity V_c as a function of diameter (Figures 27, 28 and 29) in conjunction with equation (1), it is possible to calculate the particle size dependence of the surface tension, γ_{PV} , and of the contact angle with water, θ .

It is possible to refer the new boundary conditions to any desired temperature by using the estimated average temperature coefficient of surface tension. The boundary conditions referred to 20°C and to the melting points of thymol (51.5°C), biphenyl (70°C) and naphthalene (80°C) are indicated in Table 19. It is evident that the boundary conditions shown in Table 14 are more conclusive in nature than those in Table 19. The new boundary conditions are dependent entirely on the optimization process. The calculated particle size dependence of the surface tension, γ_{pv} , and of the contact angle, θ , should conform to these new boundary conditions listed in Table 19. The estimated average thermal conductivity k_2 conforms very well with the permissible k_2 ranges for naphthalene but is too high for large particle sizes in thymol and too low for large particle sizes in biphenyl. Therefore it is to be expected that the particle size dependence of surface tension will be overestimated by the thymol system and will be underestimated by the biphenyl system. This is borne out by the curves in Figure 40.

The particle size dependence of the surface tension, γ_{pv} , at 20°C determined from the three systems, thymol, biphenyl and naphthalene are indicated in Tables 20, 21 and 22, respectively, and in Figures 34, 35 and 36, respectively. The particle size dependence of the contact angle, θ , at 20°C determined from the thymol, biphenyl and naphthalene systems are indicated in Tables 20, 21 and 22, respectively, and in Figures 37, 38 and 39, respectively. The error bars in these

figures correspond to the velocity band width in the critical velocity, V_c , vs. particle diameter, D , plots (Figures 27, 28 and 29).

Figures 40 and 41 show the particle size dependence of the surface tension and of the contact angle, respectively, using only the critical velocity from the three systems (thymol, biphenyl and naphthalene), cf. Figures 27, 28 and 29.

The results determined from naphthalene agree very well with the boundary conditions expressed in Table 19. The results determined from biphenyl and thymol deviate as expected.

2.2 COAL SAMPLE NO. 3

The "ranking" series of engulfment experiments have indicated that for all particle sizes of coal sample No. 3 wet

$$\gamma_{pv} > 38.70 \text{ ergs/cm}^2 \text{ at } 59^\circ\text{C}$$

and

$$\theta < 69.5^\circ \text{ at } 59^\circ\text{C}.$$

The plots of critical velocity, V_c , vs. particle diameter, D , for thymol and biphenyl of coal sample No. 3 wet and coal sample No. 3 dry are shown in Figures 30, 31, 32 and 33, respectively.

The higher hydrophilicity of the dry screened sample relative to the wet screened sample is apparent in these plots. A careful study of Tables 20, 21 and 22 shows that the solidification front technique is sensitive to small changes in surface properties. For thymol a 1 erg/cm^2 difference in surface tension corresponds to a $1\text{-}2 \text{ }\mu\text{m/sec}$ change in critical velocity. For biphenyl

a 1 erg/cm^2 difference in surface tension corresponds to a change in V_c of approximately $20 \text{ } \mu\text{m/sec}$ change and for naphthalene a 1 erg/cm^2 difference in surface tension corresponds to a change in critical velocity of approximately $40 \text{ } \mu\text{m/sec}$. A comparison of Figure 30 with Figure 31 and Figure 32 with Figure 33 shows that the dry screened sample has a surface tension, γ_{PV} , which is approximately 2 ergs/cm^2 higher. This corresponds to a contact angle with water, θ , less than 62.27° .

A preliminary calculation utilizing the critical velocity, V_c , determined from biphenyl and thymol in conjunction with the equation from dimensional analysis shows that the average thermal conductivity, k_2 , for coal sample No. 3 wet is approximately $9.10^{-5} [\text{cal/sec.cm}^\circ\text{K}]$.

SUMMARY OF CONCLUSIONS

1. The freezing front technique has been proven to be a powerful method for the characterization of surface properties of coal particles.
2. This technique has two levels:
 - a) Level 1 consists of the "ranking" of the coal samples in comparison with the surface tension, γ_{LV} , of organic matrix materials. Since the condition for particle engulfment at arbitrarily small values of the rate of solidification is $\gamma_{PV} < \gamma_{LV}$, it is possible to determine the range of the surface tension, γ_{PV} , by performing a series of engulfing experiments with matrix materials of different surface tension, γ_{LV} . The technique yields ranges, given by the differences in the γ_{LV} values of the matrix materials, in which the γ_{PV} values of the particles must lie. The corresponding contact angle ranges are easily calculated. Although several matrix materials are required, the measurements are easily and quickly performed. By suitable choices of the matrix materials, the above ranges can be made very small.
 - b) Level 2 essentially consists in the determination of the critical velocity of engulfing, V_c , of an individual particle by a suitable matrix material. The free energy of adhesion ΔF^{adh} can be obtained from V_c by means of a scheme of dimensional analysis,

and surface tensions and contact angles in turn can be obtained from ΔF^{adh} using equation of state relations. The technique is capable of very high accuracy and is suitable to study, e.g. the change of wettability with particle size.

However, the knowledge of several physical properties of the test particles is required, i.e. density, specific heat and thermal conductivity. Level 2, though time consuming at the present state of development, is amenable to automation by means of image analysis and television video techniques.

3. The surface tensions, γ_{PV} , and contact angles with water, θ , at 20°C as obtained from the level 1 investigation are summarized as follows:

COAL SAMPLE NO.	SURFACE TENSION, γ_{PV} [ergs/cm ²]	CONTACT ANGLE, θ [DEGREES]
1	≤ 31.9	≥ 85.3
2	$36.8 \leq \gamma_{\text{PV}} \leq 41.2$	$70.2 \leq \theta \leq 77.6$
3 wet	≥ 41.2	≤ 70.2
3 dry	≥ 43.2	≤ 66.9

4. The results of level 2 studies show that the surface tension, γ_{PV} , as well as the contact angle with water are different for different particle sizes. Thus, for coal sample No. 2, from the smallest to the largest particles investigated the surface tension increases by approximately

3 ergs/cm² and the contact angle correspondingly decreases by approximately 4 degrees.

5. The results for the surface properties for the coal samples were supported qualitatively by the determination of moisture and ash content, specific heat, density, surface area and mineral composition of the coal samples. These quantities show variations with particle size consistent with those of the surface tensions, γ_{py} and contact angles, θ .

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TABLE 1 FRACTION SIZES IN MESH AND IN MICROMETER

FRACTION NUMBER	MESH	MICRON [μm]	EFFECTIVE DIAMETER [μm]
1	-60 ⁺ (-65) [*]	<235(<208)	-
2	60-100	147-235	191
3	100-150	104-147	125
4	150-200	74-104	89
5	200-325	45-74	60
6	325-400	37-45	41
7	-400	<37	-

⁺ Coal Sample No.1 and No.2

^{*} Coal Sample No.3

TABLE 2 DENSITY VALUES OF COAL SAMPLES

FRACTION OF COAL [MESH]	DENSITY [g/cm ³]		
	SAMPLE NO.1	SAMPLE NO.2	SAMPLE NO.3
-60(-65)	1.42	1.42	1.70
60-100	1.52	1.47	1.63
100-150	1.36	1.44	1.70
150-200	1.32	1.41	1.65
200-325	1.43	1.43	1.64
325-400	1.34	1.41	1.65
-400	1.35	1.45	1.94

These data were obtained from EMR Western Research Laboratories, Edmonton, Alberta, courtesy of Dr. H. Hamza.

TABLE 3 COAL SAMPLE NO.1 WET SCREENED

TEMPERATURE [°K]	SPECIFIC HEAT c_p [Cal/(g°K)] MESH SIZE OF FRACTIONS 60-100
300	0.2405
310	0.2654
320	0.2892
330	0.2957
340	0.3053
350	0.2983
360	0.3012

TABLE 4 COAL SAMPLE NO.2 WET SCREENED

TEMPERATURE [°K]	SPECIFIC HEAT C_p [Cal/(g°K)]						
	MESH SIZE OF FRACTIONS						
	60-100	100-150	150-200	200-325	325-400	-400	
300	0.2664	0.2652	0.2468	0.2414	0.2487	0.2510	
310	0.2709	0.2835	0.2657	0.2627	0.2664	0.2854	
320	0.2852	0.3009	0.2951	0.2830	0.2943	0.3312	
330	0.2916	0.3077	0.3144	0.3027	0.3354	0.3388	
340	0.2912	0.3193	0.3261	0.3155	0.3465	0.3649	
350	0.2945	0.3120	0.3186	0.3083	0.3386	0.3565	
360	0.2977	0.3164	0.3230	0.3014	0.3311	0.3486	

TABLE 5 COAL SAMPLE NO.3 WET SCREENED

TEMPERATURE [°K]	SPECIFIC HEAT C_p [Cal/(g°K)]					
	MESH SIZE OF FRACTIONS					
	65-100	100-150	150-200	200-325	325-400	-400
300	0.2999	0.2771	0.2655	0.2229	0.2044	0.2561
310	0.3342	0.3244	0.3291	0.2960	0.3224	0.3133
320	0.4197	0.4239	0.4188	0.3969	0.4453	0.4088
330	0.5384	0.5354	0.5458	0.5528	0.5426	0.5254
340	0.6559	0.6617	0.6792	0.6457	0.6344	0.6582
350	0.7144	0.7468	0.7716	0.6619	0.6702	0.7377
360	0.7350	0.7440	0.7777	0.6318	0.6382	0.8335

TABLE 6 COAL SAMPLE NO.3 DRY SCREENED

TEMPERATURE [°K]	SPECIFIC HEAT C_p [Cal/(g°K)]					
	MESH SIZE OF FRACTIONS					
	65-100	100-150	150-200	200-325	325-400	-400
300	0.2811	0.2915	0.2668	0.2661	0.2456	0.2418
310	0.3674	0.3558	0.3648	0.3706	0.3324	0.3536
320	0.5179	0.4694	0.5081	0.5408	0.4689	0.5140
330	0.7565	0.6441	0.7146	0.7605	0.6622	0.7255
340	0.9695	0.8415	0.9172	0.9759	0.8474	0.9393
350	1.0926	1.0259	1.0590	1.1276	1.0205	1.1088
360	1.0758	1.1305	1.0919	1.1811	1.1248	1.1997

TABLE 7 MOISTURE CONTENT OF COAL SAMPLES

FRACTION OF COAL [MESH]	MOISTURE CONTENT [%]			
	WET SCREENED			DRY SCREENED
	SAMPLE No.1	SAMPLE No.2	SAMPLE No.3	SAMPLE No.3
-60 (-65)	1.70	1.32	2.51	9.57
60-100	0.10	0.47	2.33	10.43
100-150	0.10	0.40	3.57	10.55
150-200	0.24	0.49	2.85	9.95
200-325	1.45	0.64	2.40	9.47
325-400	0.30	0.62	1.59	8.77
-400	0.50	9.00	1.45	8.75

TABLE 8 ASH CONTENT OF COAL SAMPLES

FRACTION OF COAL [MESH]	ASH CONTENT [%]			
	WET SCREENED			DRY SCREENED SAMPLE NO.3
	SAMPLE NO.1	SAMPLE NO.2	SAMPLE NO.3	
-60 (-65)	12.39	20.16	32.24	36.03
60-100	19.38	23.33	28.96	31.03
100-150	14.07	17.55	28.85	32.36
150-200	12.26	18.87	30.01	37.18
200-325	10.78	17.03	31.71	39.11
325-400	11.61	16.57	32.23	41.47
-400	11.63	21.21	38.79	42.33

These data were obtained from EMR Western Research Laboratories,
Edmonton, Alberta, courtesy of Dr. H. Hamza

TABLE 9 SURFACE AREA OF COAL SAMPLES

FRACTION OF COAL [MESH]	SURFACE AREA [m ² /g]		
	SAMPLE NO.1	SAMPLE NO.2	SAMPLE NO.3
-60 (-65)	2.06	2.17	9.51
60-100	0.55	0.62	10.43
100-150	0.44	0.46	10.65
150-200	0.41	0.35	11.84
200-325	0.72	0.89	12.15
325-400	0.69	0.35	12.37
-400	4.29	1.67	14.63

These data were obtained from EMR Western Research Laboratories,
Edmonton, Alberta, courtesy of Dr. H. Hamza

TABLE 10 MINERAL COMPOSITION OF COAL SAMPLE NO.1 AND NO.2
(ELEMENT IN ppm UNLESS NOTED)

ELEMENT		MESH SIZE OF COAL FRACTIONS							NSB* -SRM STANDARD COAL	LITER- ATURE* DATA FOR AVERAGE COAL
SAMPLE NO.		-60	60-100	100-150	150-200	200-325	325-400	-400		
Al%	1	1.02	1.57	1.24	1.03	0.87	0.79	0.97	1.51 ± 0.08	1.85 ± 0.13
	2	2.05	2.45	2.01	1.85	1.69	1.71	2.13		
Ca%	1	0.46	0.47	0.44	0.40	0.37	0.42	0.51	0.37 ± 0.04	0.43 ± 0.05
	2	0.76	0.76	0.61	0.63	0.66	0.69	0.85		
Mg%	1	0.32	0.42	0.33	0.29	0.23	0.26	0.27	0.19 ± 0.04	0.20 ± 0.05
	2	0.53	0.61	0.52	0.46	0.44	0.45	0.59		
Na%	1	0.091	0.115	0.109	0.099	0.084	0.086	0.068	0.036±0.002	0.041± 0.002
	2	0.145	0.164	0.140	0.131	0.122	0.120	0.139		
Ti	1	564	857	674	583	508	542	611	920 ± 50	1110 ± 100
	2	1085	1162	973	972	956	964	1000		
Mn	1	7.8	10.3	8.5	6.5	7.1	8.3	12.4	41 ± 2	40 ± 3
	2	58	90	60	45	40	37	59		
U	1	1.5	1.9	1.7	1.6	1.5	1.5	1.6	1.6 ± 0.2	1.4 ± 0.1
	2	2.0	2.0	2.0	2.0	2.0	2.0	1.9		
Dy	1	0.79	0.91	0.80	0.75	0.68	0.76	0.77	0.57 ± 0.04	0.49 ± 0.08
	2	1.25	1.30	1.23	1.23	1.16	1.15	1.23		
Sr	1	182	189	186	177	199	193	209	120 ± 20	161 ± 16
	2	189	175	164	160	177	164	182		
Ba	1	1329	1280	1308	1251	1147	1169	1505	320 ± 20	352 ± 30
	2	730	677	581	594	562	565	830		
V	1	46	60	50	44	40	40	45	32.3 ± 1.5	35 ± 3
	2	29	30	26	27	25	26	30		
Cl	1	507	455	525	553	517	532	494	920 ± 30	890 ± 125
	2	144	125	130	165	160	171	141		

* R.G.V. HANCOCK: Low Flux Multielement Instrumental Neutron Activation Analysis
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TABLE 11. MINERAL COMPOSITION OF COAL SAMPLE NO. 3 WET AND DRY SCREENED
(ELEMENT IN ppm UNLESS NOTED)

ELEMENT		MESH SIZE OF COAL FRACTIONS									
		-65	65-100	100-150	150-200	200-325	325-400	-400			
Al%	W	2.62	2.57	2.56	2.78	3.03	2.93	3.51			
	D	2.60	2.51	2.89	3.21	3.40	3.64	4.39			
Ca%	W	1.37	1.49	1.54	1.55	1.62	1.51	1.56			
	D	1.16	1.21	1.22	1.27	1.22	1.34	1.36			
Mg%	W	0.58	0.63	0.60	0.64	0.68	0.72	0.83			
	D	0.56	0.57	0.62	0.77	0.83	0.86	0.91			
Na%	W	0.146	0.121	0.105	0.105	0.116	0.100	0.155			
	D	0.254	0.268	0.274	0.288	0.294	0.309	0.286			
Ti	W	1056	1065	1121	1200	1233	1113	1313			
	D	930	1174	1135	1189	1211	1167	1223			
Mn	W	182	169	131	162	168	164	210			
	D	167	145	147	172	181	201	201			
U	W	4.6	4.7	5.0	4.8	4.8	5.0	5.1			
	D	4.3	4.8	4.7	5.1	5.0	5.0	5.0			
Dy	W	2.33	2.53	2.60	2.62	2.57	2.65	2.98			
	D	2.30	2.34	2.47	2.65	2.71	2.96	2.78			
Sr	W	185	181	191	185	203	172	223			
	D	165	171	146	206	217	153	171			
Ba	W	493	505	563	573	629	639	1242			
	D	454	479	454	893	1045	1272	1288			
V	W	14.5	13.6	14.6	14.0	12.3	13.7	13.2			
	D	12.5	13.6	14.3	14.2	13.8	17.0	17.0			
Cl	W	52.8	49.3	49.2	56.5	53.9	60.4	62.1			
	D	42.7	49.8	35.5	48.2	61.3	47.1	55.7			
Br	W	41.1	42.5	39.8	38.2	36.3	40.1	39.3			
	D	59.0	64.2	63.7	63.6	63.1	62.5	59.4			

TABLE 12. THERMAL AND PHYSICAL PROPERTIES OF ORGANIC MATRIX MATERIALS

SUBSTANCE	DENSITY [g/cm ³]	VISCOSITY [Poise].	SPECIFIC HEAT [cal/g °K]	THERMAL CONDUCTIVITY [cal/(sec-cm-°K)]	SURFACE TENSION γ_{lv} , at melting point [ergs/cm ²]
PINACOL	0.976				28.12 at 43.5°C
THYMOL	0.925	0.0397	0.566	0.00031	29.90 at 51.5°C
BIPHENYL	0.992	0.01490	0.440	0.00034	32.45 at 70°C
NAPHTHALENE	0.978	0.00967	0.402	0.00054	32.80 at 80°C
SALOL	1.200	0.00746	0.391	0.00020	35.30 at 43°C
2-PHENYL PHENOL	1.210				38.70 at 59.0°C

TABLE 13. CONCLUSIONS REGARDING THE "RANKING" SERIES
OF ENGULFING EXPERIMENTS FOR COAL SAMPLE NO. 1

FRACTION SIZE [mesh]	SURFACE TENSION, γ_{PV} [ergs/cm ²]	CONTACT ANGLE OF WATER, θ [degrees]
ALL	$\gamma_{PV} < 29.90$ at 51.5°C	$\theta > 82.73$ at 51.5°C

TABLE 14. CONCLUSIONS REGARDING THE "RANKING" SERIES
OF ENGULFING EXPERIMENTS FOR COAL SAMPLE NO. 2

FRACTION SIZE [mesh]	SURFACE TENSION, γ_{pv} [ergs/cm ²]	CONTACT ANGLE OF WATER, θ [degrees]
ALL	$\gamma_{pv} > 35.30$ at 43°C	$\theta < 75.29$ at 43°C
ALL	$\gamma_{pv} < 38.70$ at 59°C	$\theta > 65.72$ at 59°C

TABLE 15. CONCLUSIONS REGARDING THE "RANKING" SERIES OF
ENGULFING EXPERIMENT FOR COAL SAMPLE NO. 3 WET

FRACTION SIZE [mesh]	SURFACE TENSION, γ_{PV} [ergs/cm ²]	CONTACT ANGLE OF WATER, θ [degrees]
ALL	$\gamma_{PV} > 38.70$ at 59°C	$\theta < 65.72$ at 59°C

TABLE 16. CONCLUSIONS REGARDING THE "RANKING" SERIES OF
ENGULFING EXPERIMENT FOR COAL SAMPLE NO. 3 DRY

FRACTION SIZE [mesh]	SURFACE TENSION, γ_{PV} [ergs/cm ²]	CONTACT ANGLE OF WATER, θ [degrees]
ALL	$\gamma_{PV} > 38.70$ at 59°C	$\theta < 65.72$ at 59°C

TABLE 17. CALCULATED SURFACE TENSION, γ_{PV} , USING THE
VALUES OF THE PHYSICAL PROPERTIES IN TABLE
- FIRST ESTIMATE - (FOR COAL SAMPLE NO. 2)

FRACTION [mesh]	DIAMETER [μm]	MATRIX MATERIAL	CRITICAL VELOCITY, v_c [$\mu\text{m}/\text{sec}$]	ΔF^{adh} [ergs/cm ²]	SURFACE TENSION, γ_{PV} [ergs/cm ²]
325-400	50	THYMOL	9.13	0.8059	>64.40
		BIPHENYL	77.50	4.0580	53.75
		NAPHTHALENE	98.75	4.9982	51.00
60-100	270	THYMOL	4.85	1.1940	>64.40
		BIPHENYL	33.25	5.1461	59.05
		NAPHTHALENE	67.00	8.6416	>66.40

THYMOL

D [μm]	γ_{PV} [ergs/cm ²]	ΔF_{adh} [ergs/cm ²]	V_C [μm/sec]	$K_2 \times 10^5$ [$\frac{\text{Cal}}{\text{sec/cm}^2\text{K}}$]	D [μm]	γ_{PV} [ergs/cm ²]	ΔF_{adh} [ergs/cm ²]	V_C [μm/sec]	$K_2 \times 10^5$ [$\frac{\text{Cal}}{\text{sec/cm}^2\text{K}}$]
50	36.95	0.0990	6.22	3.30	270	39.19	0.1303	3.50	2.54
			9.13	2.13				4.85	1.75
			12.04	1.55				6.20	1.32

BIPHENYL

D [μm]	γ_{PV} [ergs/cm ²]	ΔF_{adh} [ergs/cm ²]	V_C [μm/sec]	$K_2 \times 10^5$ [$\frac{\text{Cal}}{\text{sec/cm}^2\text{K}}$]	D [μm]	γ_{PV} [ergs/cm ²]	ΔF_{adh} [ergs/cm ²]	V_C [μm/sec]	$K_2 \times 10^5$ [$\frac{\text{Cal}}{\text{sec/cm}^2\text{K}}$]
50	35.75	0.6258	70.00	3.50	270	37.99	1.0489	27.00	6.28
			77.50	3.11				33.25	4.95
			85.00	2.80				39.50	4.07

NAPHTHALENE

D [μm]	γ_{PV} [ergs/cm ²]	ΔF_{adh} [ergs/cm ²]	V_C [μm/sec]	$K_2 \times 10^5$ [$\frac{\text{Cal}}{\text{sec/cm}^2\text{K}}$]	D [μm]	γ_{PV} [ergs/cm ²]	ΔF_{adh} [ergs/cm ²]	V_C [μm/sec]	$K_2 \times 10^5$ [$\frac{\text{Cal}}{\text{sec/cm}^2\text{K}}$]
50	35.10	0.6362	78.00	2.96	270	37.34	1.2531	52.50	3.71
			98.75	2.26				67.00	2.81
			119.50	1.82				81.50	2.25

TABLE 19. CALCULATED SURFACE TENSION, γ_{PV} , AND CONTACT ANGLE, θ ,
VALUES FOR COAL SAMPLE NO. 2 (IN RELATION TO 2ND LEVEL
OF INVESTIGATION)

TEMPERATURE [°C]	SURFACE TENSION, γ_{PV} [ergs/cm ²]	CONTACT ANGLE, θ [degrees]
20.0	$39.00 \leq \gamma_{PV} \leq 41.24$	$70.29 \leq \theta \leq 74.00$
51.5	$36.95 \leq \gamma_{PV} \leq 39.19$	$66.62 \leq \theta \leq 70.49$
70.0	$35.75 \leq \gamma_{PV} \leq 37.99$	$64.41 \leq \theta \leq 68.30$
80.0	$35.10 \leq \gamma_{PV} \leq 37.34$	$63.20 \leq \theta \leq 67.21$

TABLE 20 CALCULATED SURFACE TENSION (γ_{PV}) AND CONTACT ANGLE OF WATER (θ)⁴⁷.
ON COAL SAMPLE NO. 2 FROM EXPERIMENTAL OBSERVATIONS WITH THYMOL

DIAMETER, D [μm]	CRITICAL VELOCITY, V_c [$\mu\text{m}/\text{sec}$]	AT 51.5 °C			AT 20°C	
		ΔF^{adh} [ergs/cm ²]	γ_{PV} [ergs/cm ²]	θ [degrees]	γ_{PV} [ergs/cm ²]	θ [degrees]
50	9.13 ± 2.91	0.1191±.026	38.40±1.89	67.98±3.26	40.45±1.89	71.63±3.13
60	8.58 ± 2.78	0.1247±.028	38.78±1.99	67.32±3.44	40.83±1.99	71.00±3.32
70	8.13 ± 2.63	0.1295±.029	39.13±2.07	66.72±3.58	41.18±2.07	70.42±3.47
80	7.75 ± 2.50	0.1349±.030	39.50±2.14	66.08±3.69	41.55±2.14	69.80±3.60
90	7.40 ± 2.30	0.1384±.030	39.76±2.13	65.64±3.66	41.81±2.13	69.36±3.57
100	7.15 ± 2.15	0.1422±.029	40.04±2.11	65.15±3.62	42.09±2.11	68.89±3.55
110	6.93 ± 1.93	0.1448±.029	40.22±2.04	64.85±3.50	42.27±2.04	68.58±3.44
120	6.70 ± 1.85	0.1476±.028	40.42±2.01	64.50±3.45	42.47±2.01	68.24±3.40
130	6.50 ± 1.75	0.1502±.028	40.60±1.99	64.19±3.41	42.65±1.99	67.94±3.37
140	6.30 ± 1.65	0.1524±.028	40.74±1.97	63.95±3.38	42.79±1.97	67.70±3.34
150	6.20 ± 1.63	0.1571±.026	41.09±2.03	63.35±3.48	43.14±2.03	67.10±3.45
160	6.10 ± 1.60	0.1603±.029	41.33±2.07	62.94±3.55	43.38±2.07	66.69±3.53
170	6.00 ± 1.60	0.1632±.030	41.53±2.14	62.60±3.67	43.58±2.14	66.35±3.65
180	5.88 ± 1.58	0.1655±.031	41.70±2.19	62.31±3.75	43.75±2.19	66.06±3.73
190	5.78 ± 1.58	0.1679±.032	41.87±2.26	62.02±3.87	43.92±2.26	65.76±3.85
200	5.65 ± 1.55	0.1694±.032	41.98±2.30	61.83±3.94	44.03±2.30	65.58±3.92
210	5.55 ± 1.55	0.1714±.032	42.12±2.36	61.59±4.04	44.17±2.36	65.34±4.02
220	5.45 ± 1.55	0.1731±.034	42.24±2.42	61.38±4.16	44.29±2.42	65.13±4.14
230	5.33 ± 1.50	0.1742±.034	42.32±2.42	61.25±4.14	44.37±2.42	64.99±4.12
240	5.20 ± 1.45	0.1748±.034	42.37±2.40	61.16±4.11	44.42±2.40	64.91±4.10
250	5.08 ± 1.45	0.1755±.035	42.41±2.46	61.09±4.22	44.46±2.46	64.84±4.20
260	4.95 ± 1.40	0.1757±.034	42.43±2.45	61.06±4.19	44.48±2.45	64.80±4.17
270	4.85 ± 1.35	0.1765±.034	42.48±2.42	60.97±4.14	44.53±2.42	64.72±4.13

TABLE 21 CALCULATED SURFACE TENSION (γ_{PV}) AND CONTACT ANGLE OF WATER (θ) 48.
ON COAL SAMPLE NO.2 FROM EXPERIMENTAL OBSERVATIONS WITH BIPHENYL

DIAMETER, D [μm]	CRITICAL VELOCITY, V_c [$\mu\text{m}/\text{sec}$]	AT 70°C			AT 20°C	
		ΔF_{adh} [ergs/cm ²]	γ_{PV} [ergs/cm ²]	θ [degrees]	γ_{PV} [ergs/cm ²]	θ [degrees]
50	77.5 $\pm$ 7.50	0.5998 $\pm$.040	35.60 $\pm$ 0.20	68.59 0.36	38.85 $\pm$ 0.20	74.26 $\pm$ 0.34
60	73.5 $\pm$ 7.50	0.6289 $\pm$.047	35.76 $\pm$ 0.25	68.31 0.44	39.01 $\pm$ 0.25	74.00 $\pm$ 0.41
70	71.75 $\pm$ 7.50	0.6696 $\pm$.048	35.97 $\pm$ 0.26	67.94 $\pm$ 0.45	39.22 $\pm$ 0.26	73.66 $\pm$ 0.42
80	66.25 $\pm$ 7.25	0.6735 $\pm$.051	35.99 $\pm$ 0.26	67.91 $\pm$ 0.47	39.24 $\pm$ 0.26	73.63 $\pm$ 0.44
90	62.00 $\pm$ 7.00	0.6813 $\pm$.053	36.04 $\pm$ 0.28	67.82 $\pm$ 0.48	39.29 $\pm$ 0.28	73.54 $\pm$ 0.45
100	58.50 $\pm$ 6.50	0.6890 $\pm$.053	36.08 $\pm$ 0.28	67.75 $\pm$ 0.48	39.33 $\pm$ 0.28	73.48 $\pm$ 0.46
110	56.00 $\pm$ 6.00	0.6990 $\pm$.057	36.12 $\pm$ 0.27	67.68 $\pm$ 0.47	39.37 $\pm$ 0.27	73.41 $\pm$ 0.44
120	53.00 $\pm$ 6.00	0.7021 $\pm$.055	36.15 $\pm$ 0.28	67.63 $\pm$ 0.50	39.40 $\pm$ 0.28	73.36 $\pm$ 0.47
130	50.00 $\pm$ 6.00	0.70131 $\pm$.058	36.14 $\pm$ 0.31	67.64 $\pm$ 0.54	39.39 $\pm$ 0.31	73.38 $\pm$ 0.51
140	48.00 $\pm$ 6.00	0.7069 $\pm$.061	36.17 $\pm$ 0.32	67.59 $\pm$ 0.56	39.42 $\pm$ 0.32	73.33 $\pm$ 0.52
150	46.25 $\pm$ 6.25	0.7174 $\pm$.067	36.23 $\pm$ 0.35	67.49 $\pm$ 0.61	39.48 $\pm$ 0.35	73.23 $\pm$ 0.58
160	44.25 $\pm$ 6.25	0.7181 $\pm$.070	36.23 $\pm$ 0.36	67.49 $\pm$ 0.64	39.48 $\pm$ 0.36	73.23 $\pm$ 0.60
170	43.00 $\pm$ 6.00	0.7251 $\pm$.070	36.27 $\pm$ 0.39	67.42 $\pm$ 0.66	39.52 $\pm$ 0.37	73.16 $\pm$ 0.61
180	41.75 $\pm$ 6.25	0.7305 $\pm$.075	36.29 $\pm$ 0.40	67.38 $\pm$ 0.71	39.54 $\pm$ 0.40	73.13 $\pm$ 0.66
190	40.00 $\pm$ 6.00	0.7282 $\pm$.075	36.29 $\pm$ 0.40	67.38 $\pm$ 0.69	39.54 $\pm$ 0.40	73.13 $\pm$ 0.65
200	39.00 $\pm$ 6.50	0.7337 $\pm$.083	36.32 $\pm$ 0.44	67.33 $\pm$ 0.79	39.57 $\pm$ 0.44	73.08 $\pm$ 0.73
210	37.75 $\pm$ 6.25	0.7346 $\pm$.084	36.32 $\pm$ 0.44	67.33 $\pm$ 0.77	39.57 $\pm$ 0.44	73.08 $\pm$ 0.72
220	36.25 $\pm$ 6.25	0.7308 $\pm$.087	36.30 $\pm$ 0.46	67.36 $\pm$ 0.81	39.55 $\pm$ 0.46	73.12 $\pm$ 0.76
230	35.25 $\pm$ 6.25	0.7325 $\pm$.089	36.31 $\pm$ 0.47	67.35 $\pm$ 0.83	39.56 $\pm$ 0.47	73.10 $\pm$ 0.78
240	34.75 $\pm$ 6.25	0.7405 $\pm$.092	36.35 $\pm$ 0.48	67.28 $\pm$ 0.85	39.60 $\pm$ 0.48	73.03 $\pm$ 0.80
250	34.25 $\pm$ 6.25	0.7478 $\pm$.094	36.39 $\pm$ 0.49	67.21 $\pm$ 0.87	39.64 $\pm$ 0.49	72.97 $\pm$ 0.82
260	33.75 $\pm$ 6.25	0.7545 $\pm$.096	36.43 $\pm$ 0.51	67.14 $\pm$ 0.89	39.68 $\pm$ 0.51	72.90 $\pm$ 0.84
270	33.25 $\pm$ 6.25	0.7606 $\pm$.098	36.46 $\pm$ 0.52	67.08 $\pm$ 0.91	39.71 $\pm$ 0.52	72.85 $\pm$ 0.86

TABLE 22 CALCULATED SURFACE TENSION (γ_{PV}) AND CONTACT ANGLE OF WATER (θ) 49.
ON COAL SAMPLE NO.2 FROM EXPERIMENTAL OBSERVATIONS WITH NAPHTHALENE

DIAMETER, D [μm]	CRITICAL VELOCITY, V_c [$\mu\text{m}/\text{sec}$]	AT 80°C			AT 20°C	
		ΔF^{adh} [ergs/cm ²]	γ_{PV} [ergs/cm ²]	θ [degrees]	γ_{PV} [ergs/cm ²]	θ [degrees]
50	98.75 $\pm$ 20.75	0.7388 $\pm$.107	35.47 $\pm$ 0.38	66.55 $\pm$ 0.68	39.37 $\pm$ 0.38	73.41 $\pm$ 0.63
60	90.25 $\pm$ 18.00	0.7587 $\pm$.104	35.54 $\pm$ 0.38	66.43 $\pm$ 0.66	39.44 $\pm$ 0.38	73.30 $\pm$ 0.62
70	84.75 $\pm$ 17.75	0.7830 $\pm$.113	35.63 $\pm$ 0.40	66.27 $\pm$ 0.72	39.53 $\pm$ 0.40	73.15 $\pm$ 0.67
80	81.50 $\pm$ 17.25	0.8094 $\pm$.118	35.72 $\pm$ 0.43	66.11 $\pm$ 0.76	39.62 $\pm$ 0.43	73.00 $\pm$ 0.71
90	79.00 $\pm$ 17.00	0.8388 $\pm$.124	35.83 $\pm$ 0.45	65.91 $\pm$ 0.80	39.73 $\pm$ 0.45	72.82 $\pm$ 0.74
100	77.00 $\pm$ 17.00	0.8673 $\pm$.132	35.93 $\pm$ 0.47	65.73 $\pm$ 0.84	39.83 $\pm$ 0.47	72.65 $\pm$ 0.79
110	75.75 $\pm$ 16.75	0.8955 $\pm$.136	36.04 $\pm$ 0.49	65.54 $\pm$ 0.88	39.94 $\pm$ 0.49	72.47 $\pm$ 0.82
120	74.75 $\pm$ 16.75	0.9256 $\pm$.143	36.14 $\pm$ 0.51	65.36 $\pm$ 0.91	40.04 $\pm$ 0.51	72.31 $\pm$ 0.85
130	74.00 $\pm$ 16.50	0.9556 $\pm$.146	36.25 $\pm$ 0.53	65.17 $\pm$ 0.94	40.15 $\pm$ 0.53	72.13 $\pm$ 0.89
140	73.50 $\pm$ 16.50	0.9859 $\pm$.152	36.36 $\pm$ 0.55	64.97 $\pm$ 0.98	40.26 $\pm$ 0.55	71.94 $\pm$ 0.92
150	72.75 $\pm$ 16.25	1.0166 $\pm$.156	36.47 $\pm$ 0.57	64.78 $\pm$ 1.00	40.37 $\pm$ 0.57	71.76 $\pm$ 0.94
160	72.25 $\pm$ 16.25	1.0439 $\pm$.162	36.57 $\pm$ 0.59	64.60 $\pm$ 1.03	40.47 $\pm$ 0.59	71.59 $\pm$ 0.97
170	72.00 $\pm$ 16.00	1.0725 $\pm$.164	36.68 $\pm$ 0.60	64.41 $\pm$ 1.05	40.58 $\pm$ 0.60	71.41 $\pm$ 0.99
180	71.25 $\pm$ 15.75	1.0947 $\pm$.166	36.76 $\pm$ 0.61	64.27 $\pm$ 1.07	40.66 $\pm$ 0.61	71.28 $\pm$ 1.01
190	70.75 $\pm$ 15.75	1.1183 $\pm$.171	36.84 $\pm$ 0.62	64.13 $\pm$ 1.09	40.74 $\pm$ 0.62	71.15 $\pm$ 1.04
200	70.50 $\pm$ 15.50	1.1437 $\pm$.173	36.94 $\pm$ 0.63	63.95 $\pm$ 1.10	40.84 $\pm$ 0.63	70.98 $\pm$ 1.05
210	69.75 $\pm$ 15.25	1.1625 $\pm$.175	37.01 $\pm$ 0.64	63.82 $\pm$ 1.12	40.91 $\pm$ 0.64	70.86 $\pm$ 1.06
220	69.25 $\pm$ 15.25	1.1831 $\pm$.179	37.08 $\pm$ 0.65	63.70 $\pm$ 1.15	40.98 $\pm$ 0.65	70.75 $\pm$ 1.08
230	68.75 $\pm$ 15.25	1.2029 $\pm$.184	37.15 $\pm$ 0.67	63.58 $\pm$ 1.18	41.05 $\pm$ 0.67	70.63 $\pm$ 1.12
240	68.50 $\pm$ 15.00	1.2249 $\pm$.185	37.23 $\pm$ 0.67	63.45 $\pm$ 1.18	41.13 $\pm$ 0.67	70.50 $\pm$ 1.12
250	67.75 $\pm$ 14.75	1.2400 $\pm$.186	37.29 $\pm$ 0.68	63.33 $\pm$ 1.20	41.19 $\pm$ 0.68	70.40 $\pm$ 1.13
260	67.25 $\pm$ 14.75	1.2574 $\pm$.190	37.35 $\pm$ 0.69	63.22 $\pm$ 1.22	41.25 $\pm$ 0.69	70.29 $\pm$ 1.15
270	67.00 $\pm$ 14.50	1.2773 $\pm$.190	37.42 $\pm$ 0.69	63.10 $\pm$ 1.22	41.32 $\pm$ 0.69	70.18 $\pm$ 1.16

FIGURE 1. DENSITY VERSUS MESH SIZE OF COAL FRACTIONS

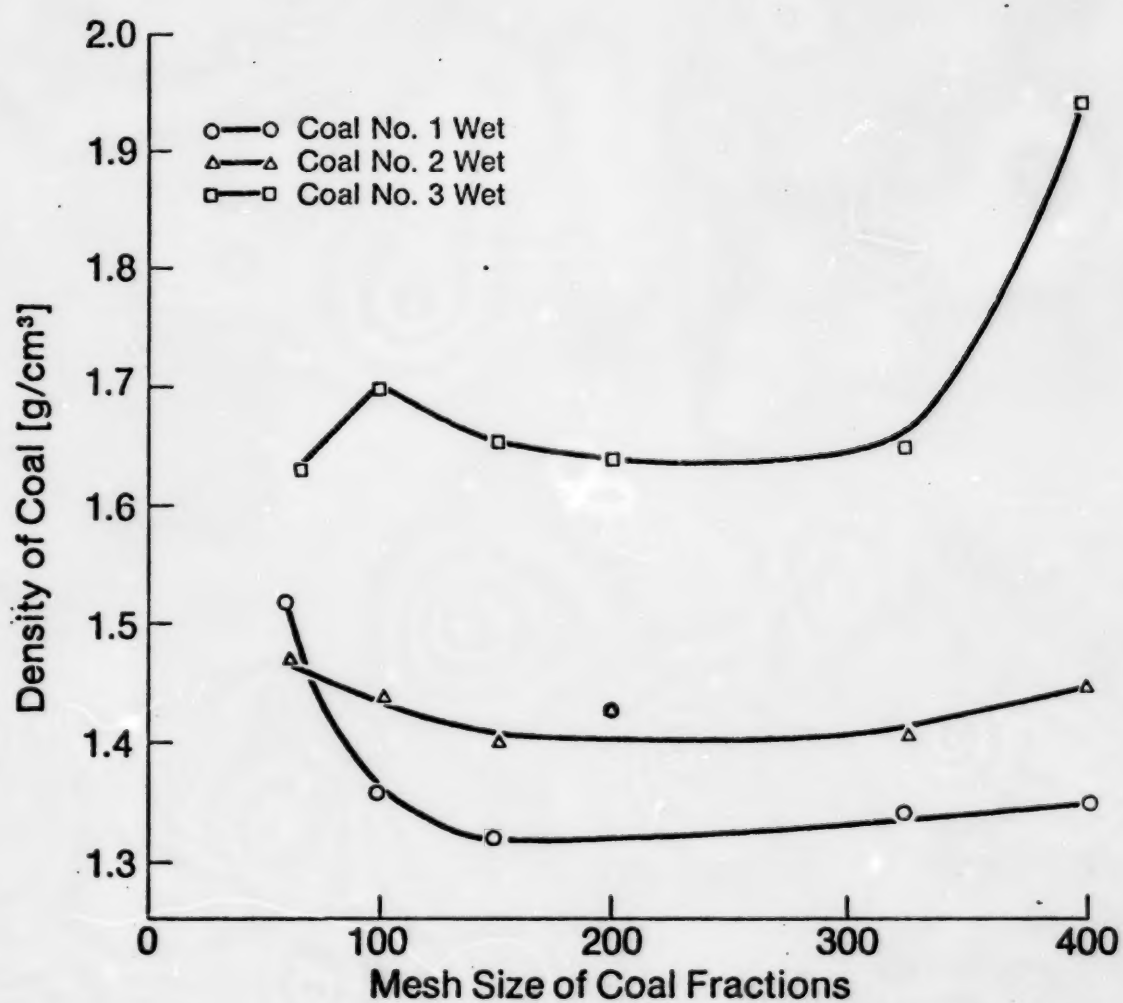


FIGURE 2. SPECIFIC HEAT VERSUS MESH
SIZE OF COAL No. 2 FRACTIONS

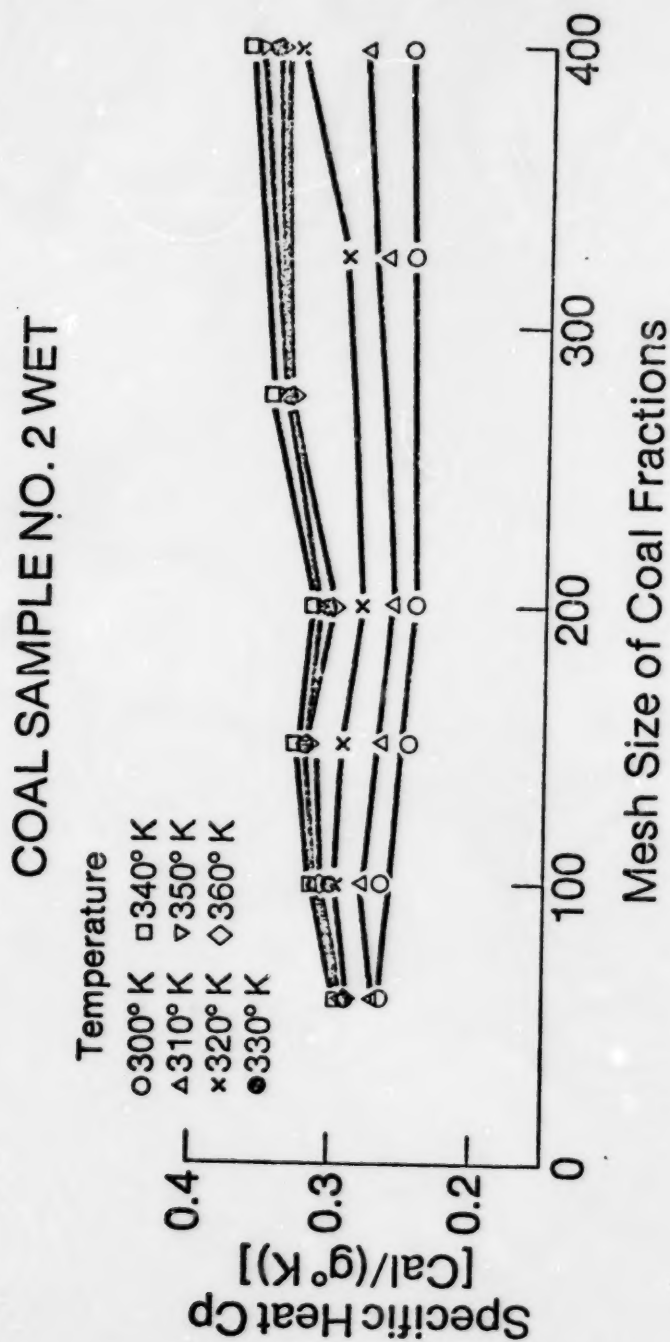


FIGURE 3. SPECIFIC HEAT VERSUS MESH SIZE
OF COAL No. 3 WET FRACTIONS

COAL SAMPLE NO. 3 WET

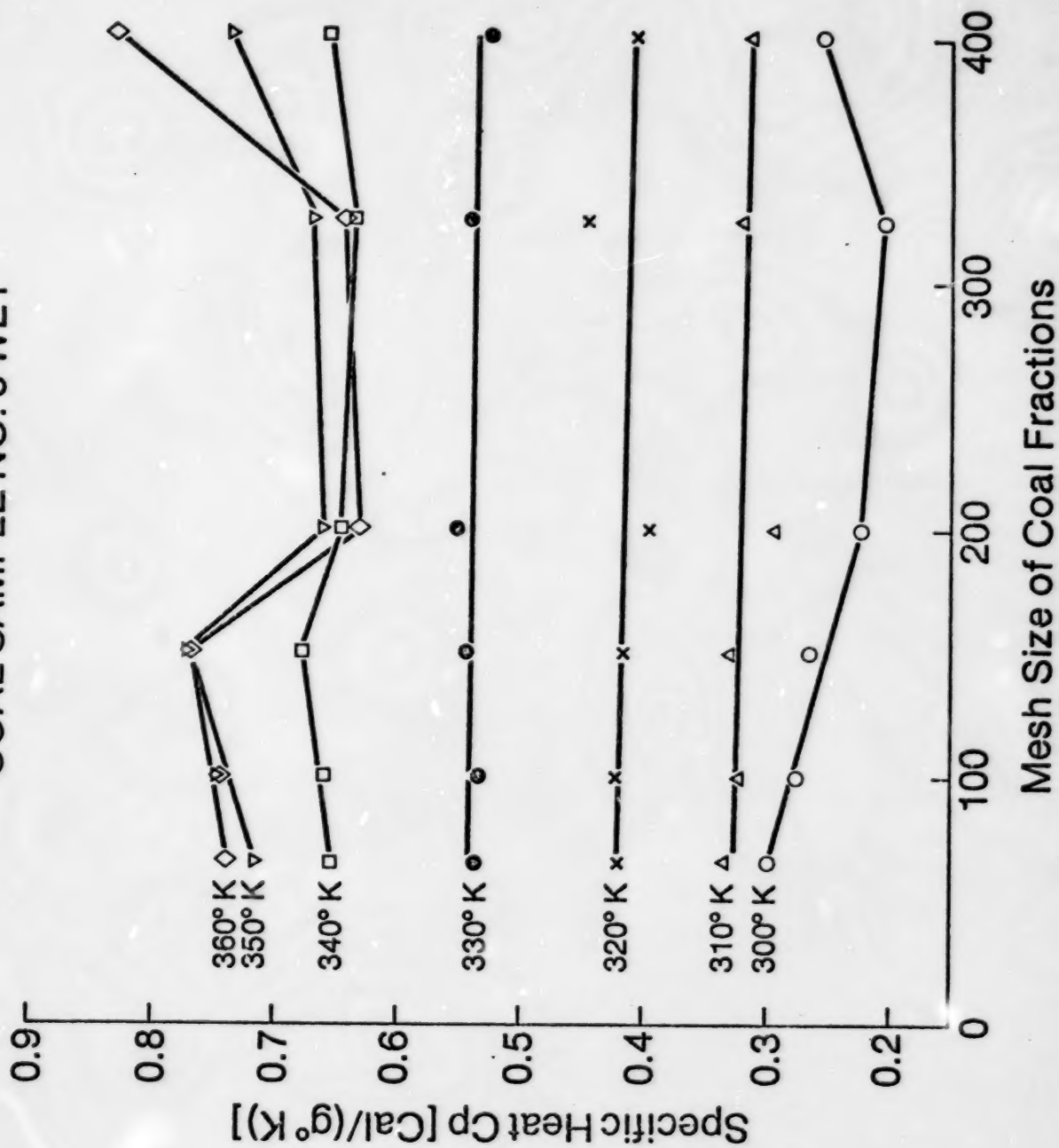


FIGURE 4. SPECIFIC HEAT VERSUS MESH SIZE
OF COAL NO. 3 DRY FRACTIONS

53.

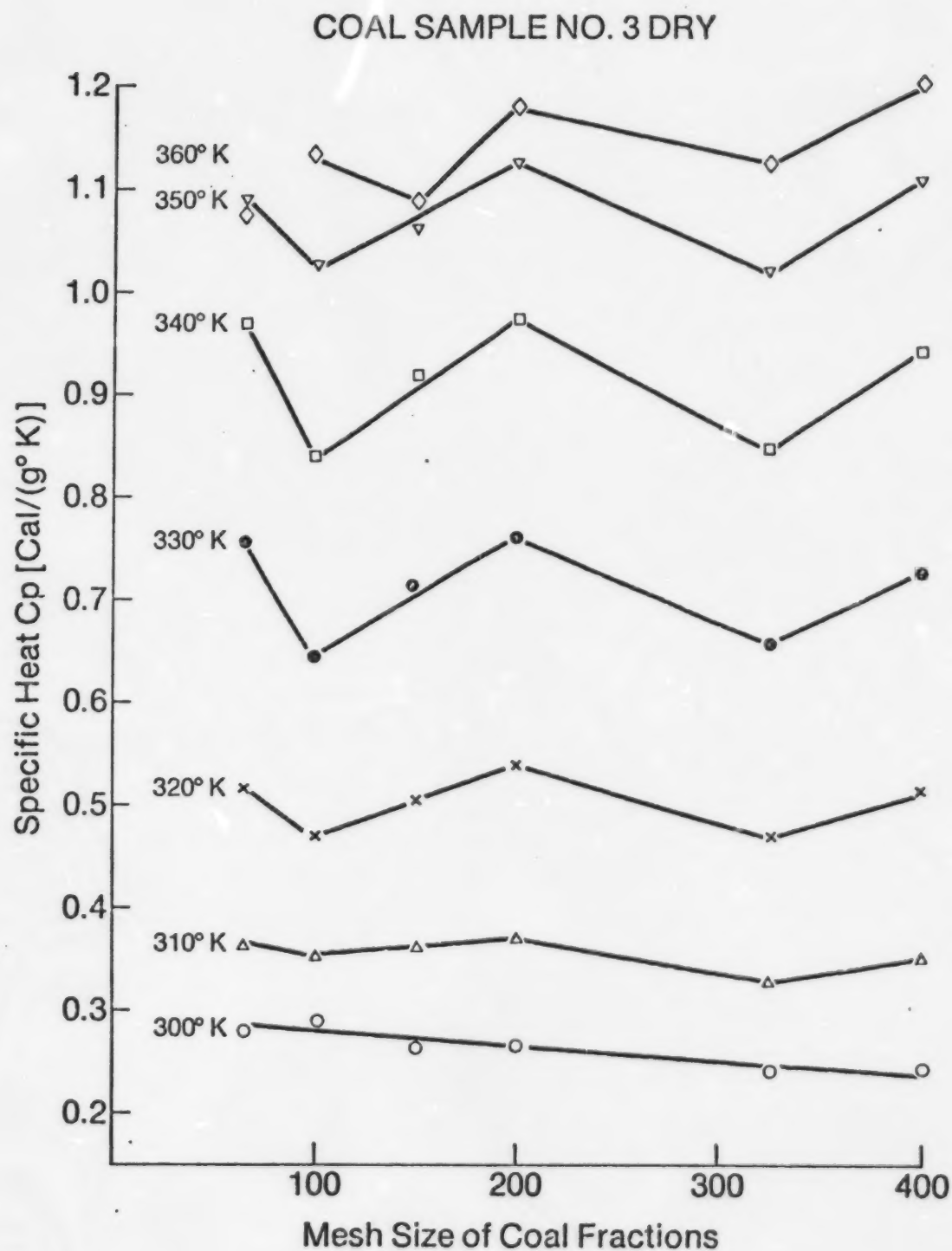


FIGURE 5, SPECIFIC HEAT VERSUS TEMPERATURE
FOR COAL SAMPLE NO. 1

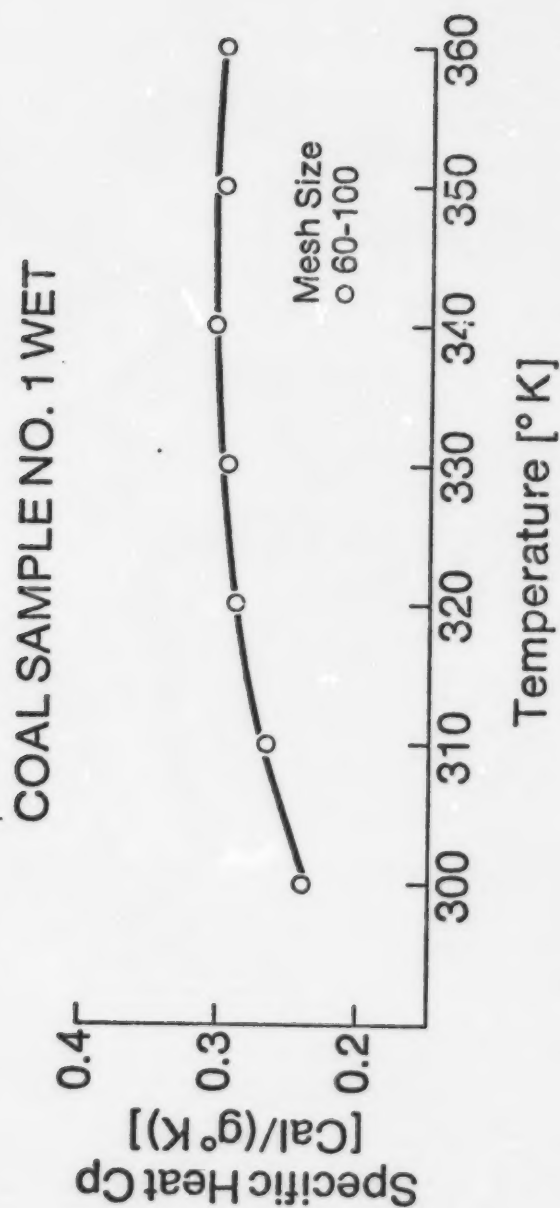


FIGURE 6. SPECIFIC HEAT VERSUS TEMPERATURE

FOR COAL SAMPLE NO. 2

COAL SAMPLE NO. 2 WET

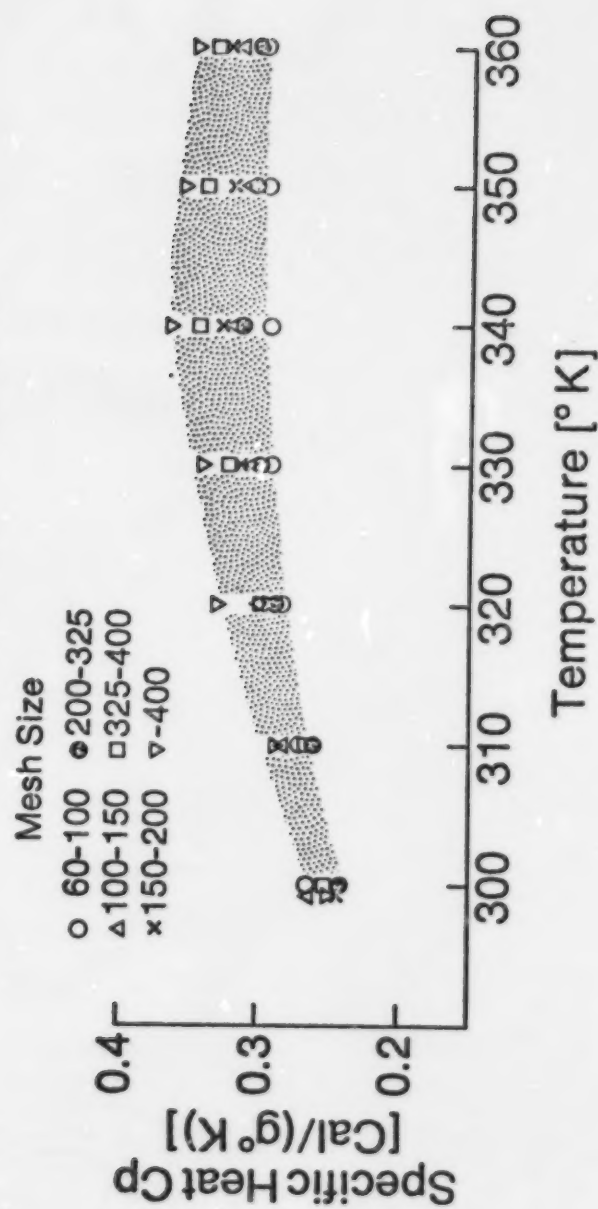


FIGURE 7. SPECIFIC HEAT VERSUS TEMPERATURE
FOR COAL SAMPLE NO. 3 WET

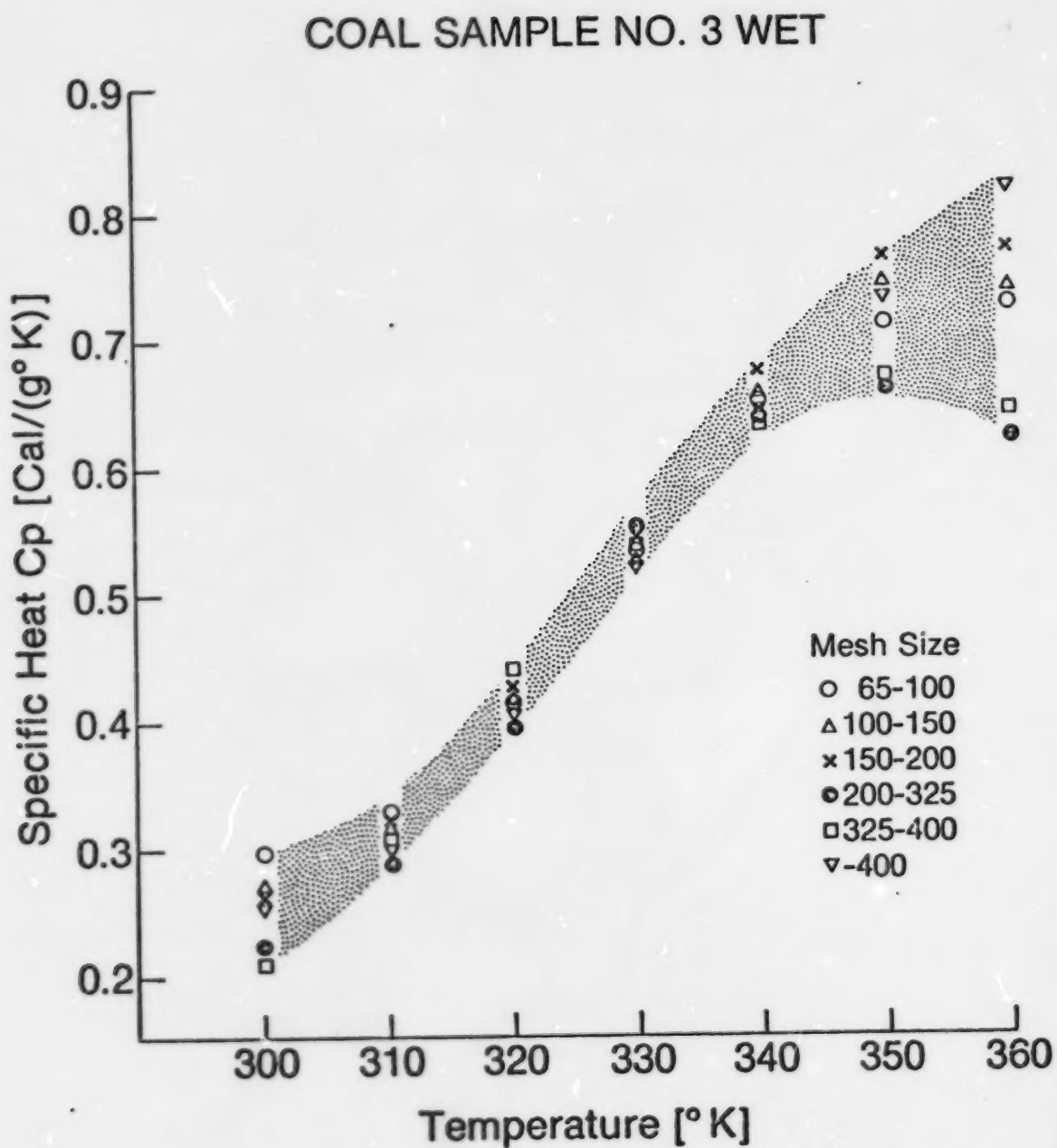


FIGURE 8, SPECIFIC HEAT VERSUS TEMPERATURE
FOR COAL SAMPLE NO. 3 DRY

57.

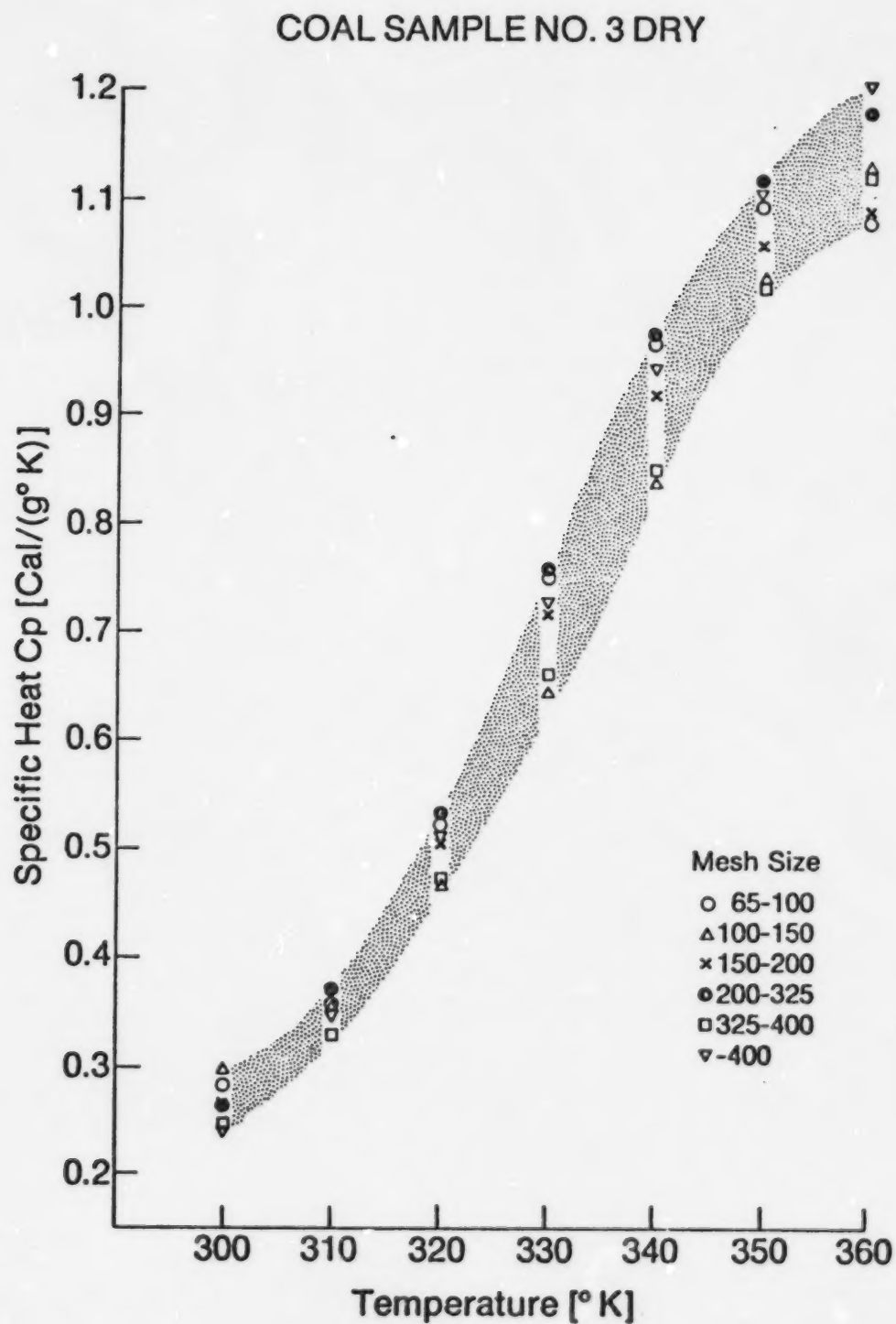


FIGURE 9. SPECIFIC HEAT VERSUS TEMPERATURE
FOR COAL FRACTIONS OF 60-100 MESH

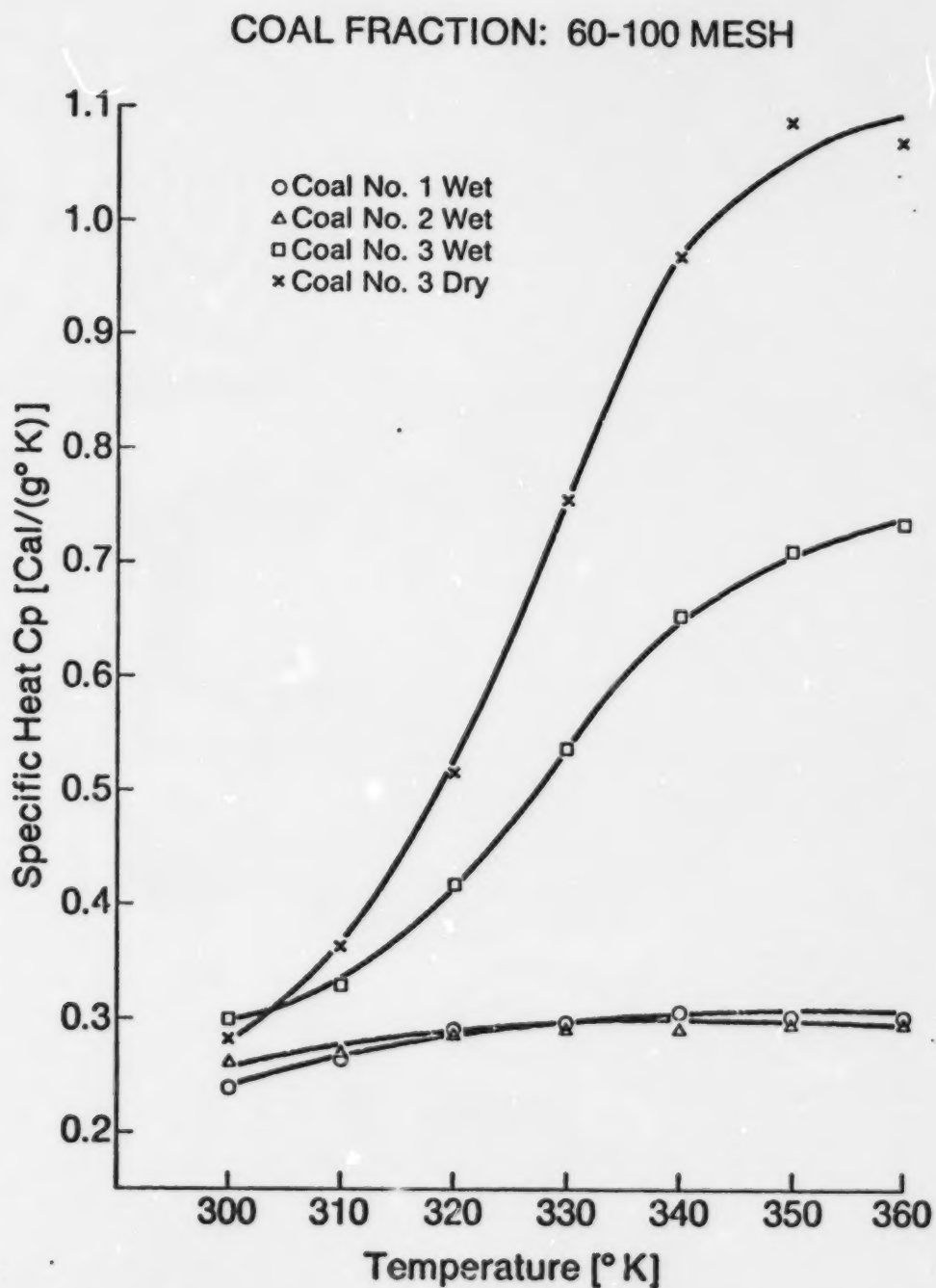


FIGURE 10, THE REPRODUCIBILITY OF SPECIFIC HEAT AS A
FUNCTION OF TEMPERATURE FOR TWO FRACTIONS
OF COAL SAMPLE NO. 3 DRY

59.

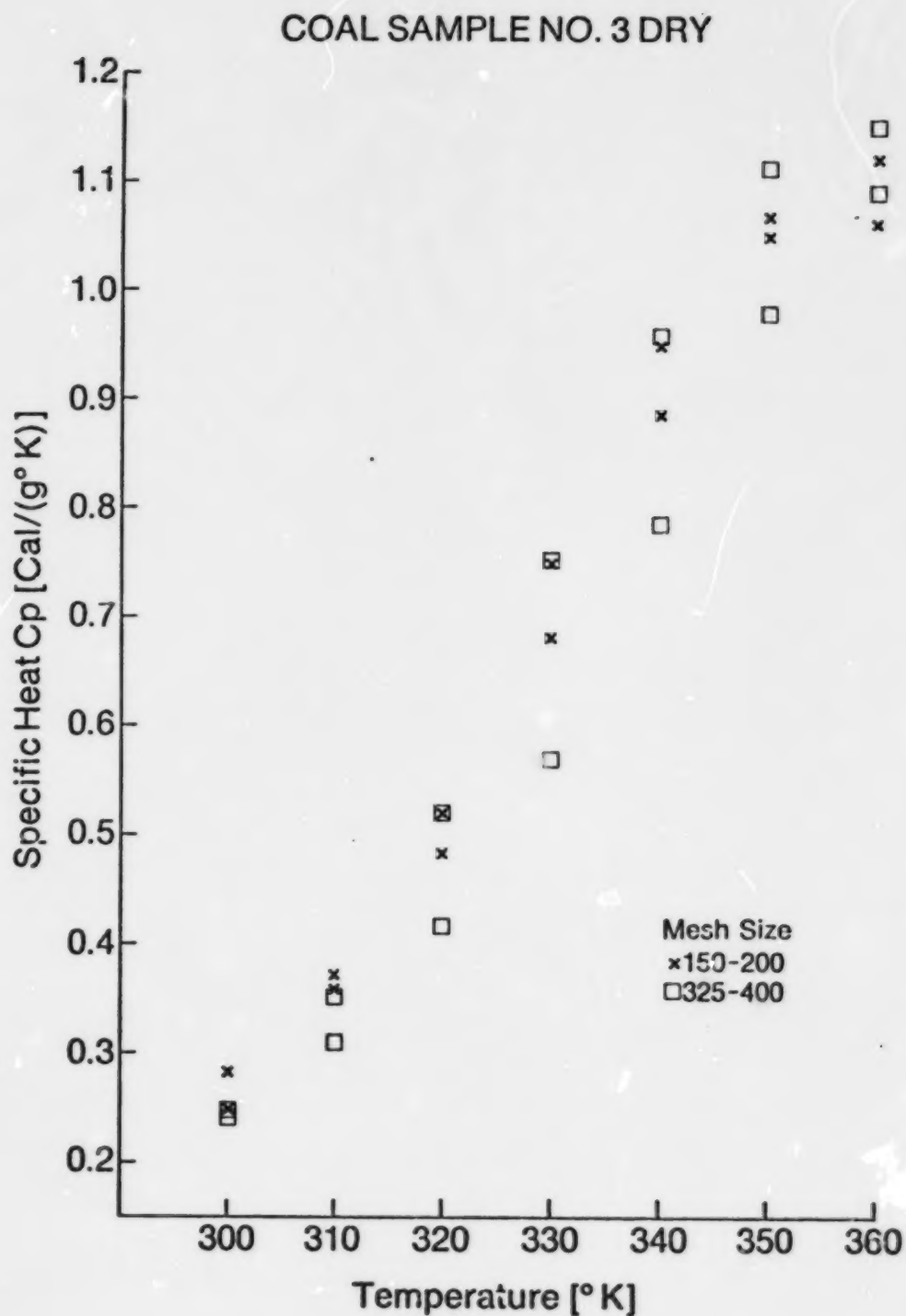


FIGURE 11. MOISTURE CONTENT VERSUS MESH SIZE OF COAL FRACTIONS

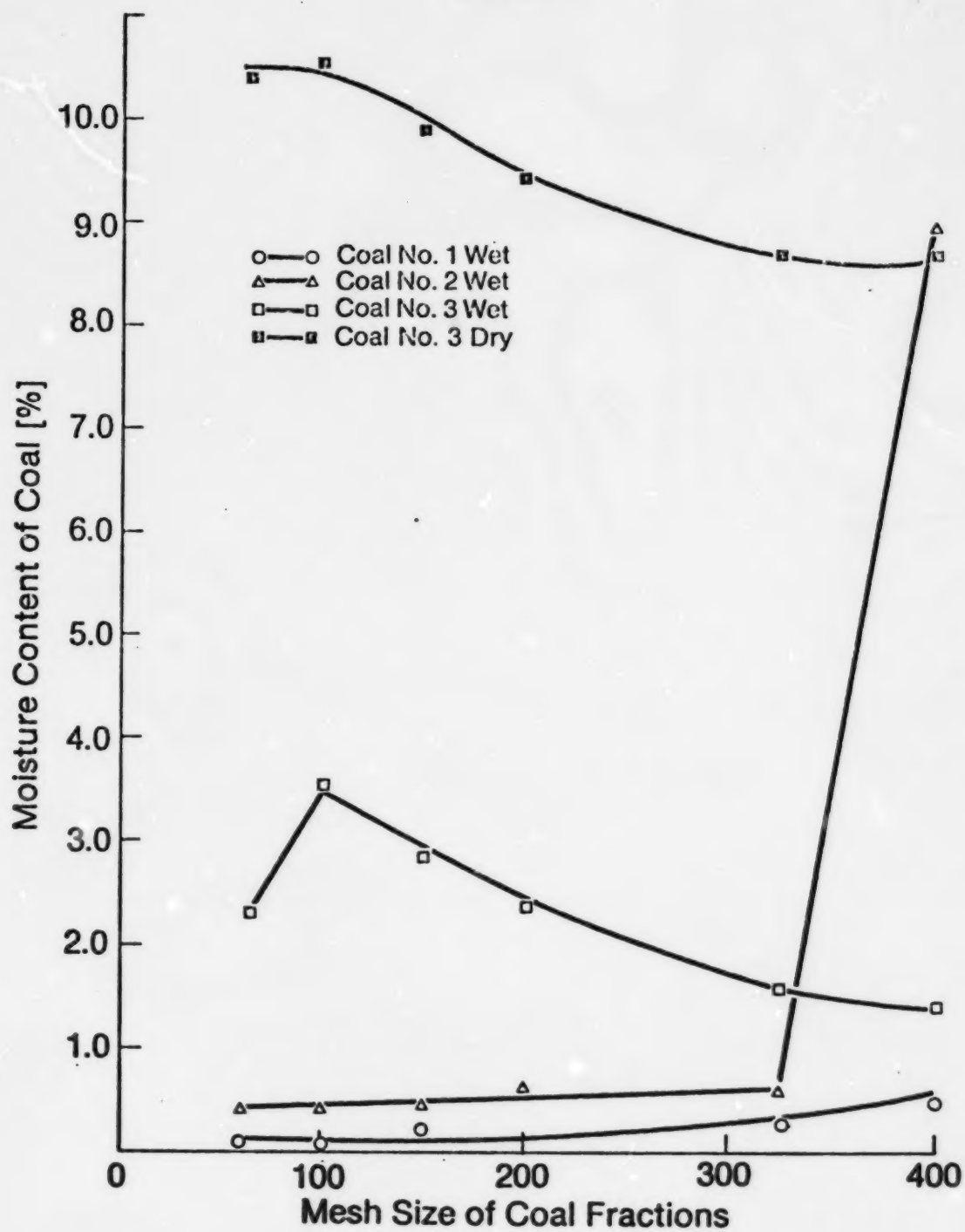


FIGURE 12. ASH CONTENT VERSUS MESH SIZE OF COAL FRACTIONS

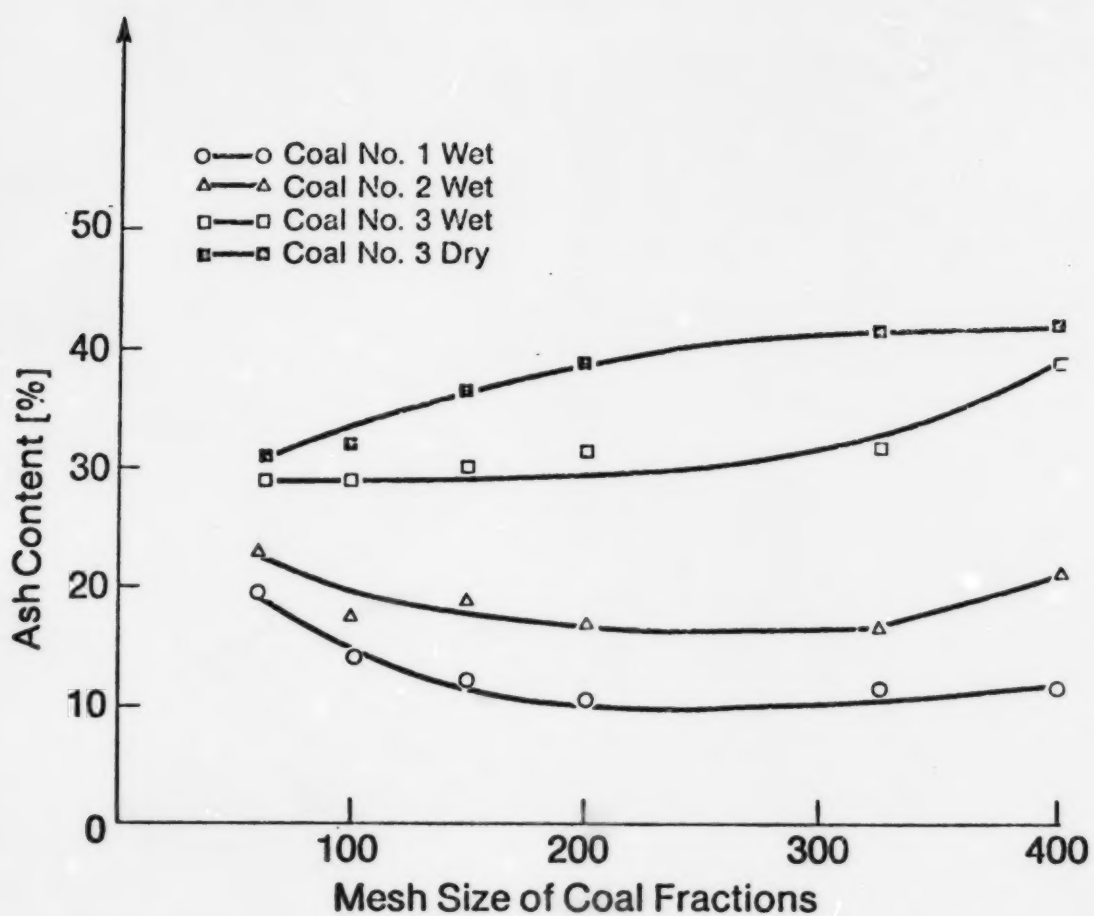


FIGURE 13. SURFACE AREA VERSUS MESH SIZE OF COAL FRACTIONS

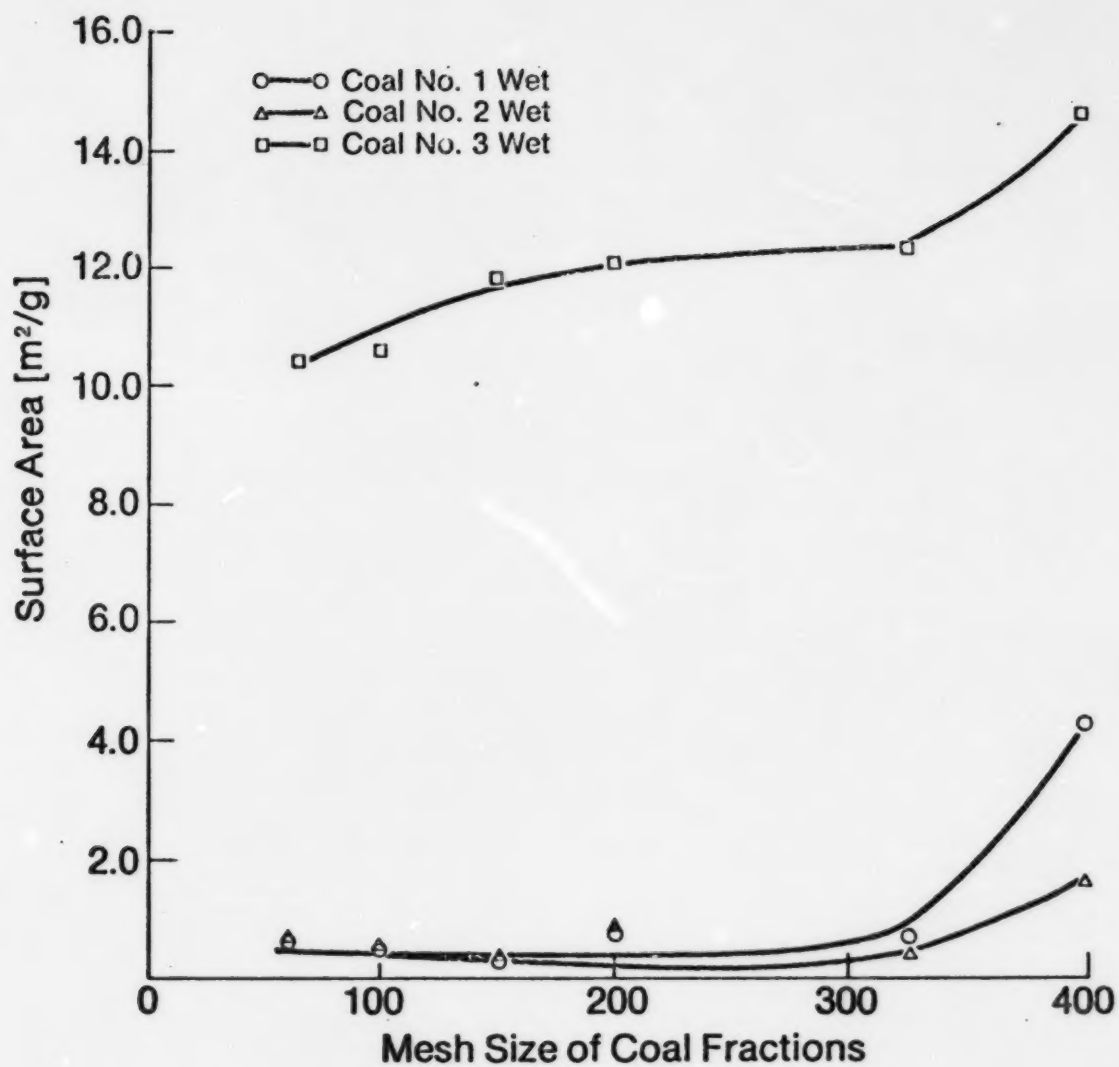


FIGURE 14. URANIUM CONTENT VERSUS MESH SIZE OF COAL FRACTIONS

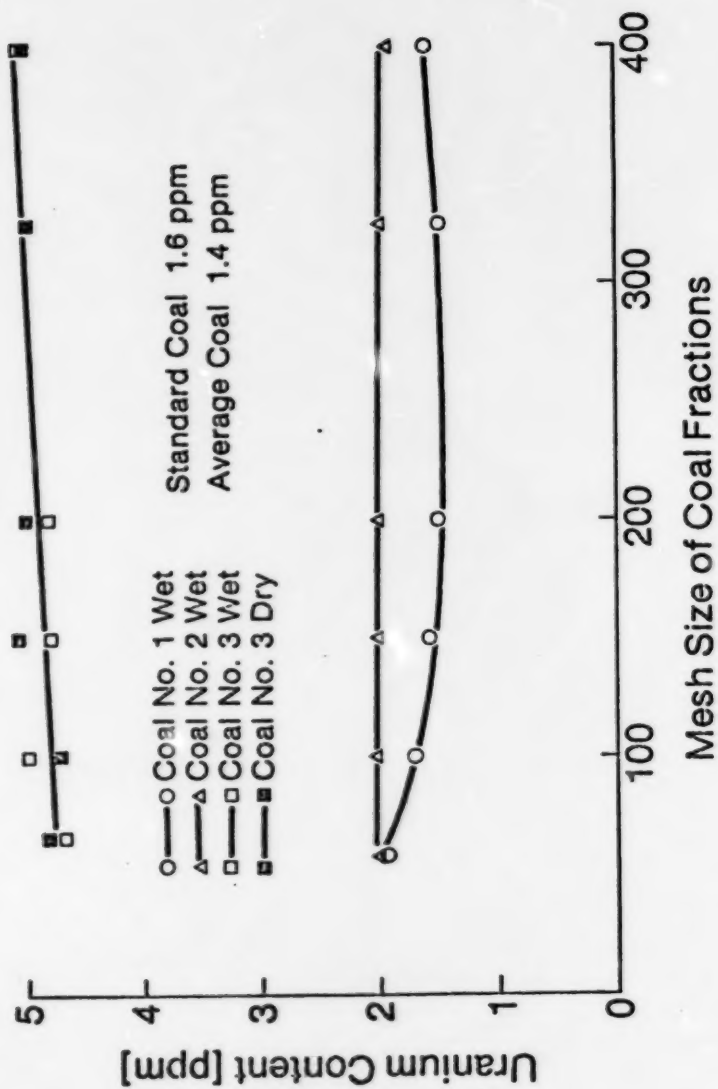


FIGURE 15. DYSPROSIUM CONTENT VERSUS MESH SIZE OF COAL FRACTIONS

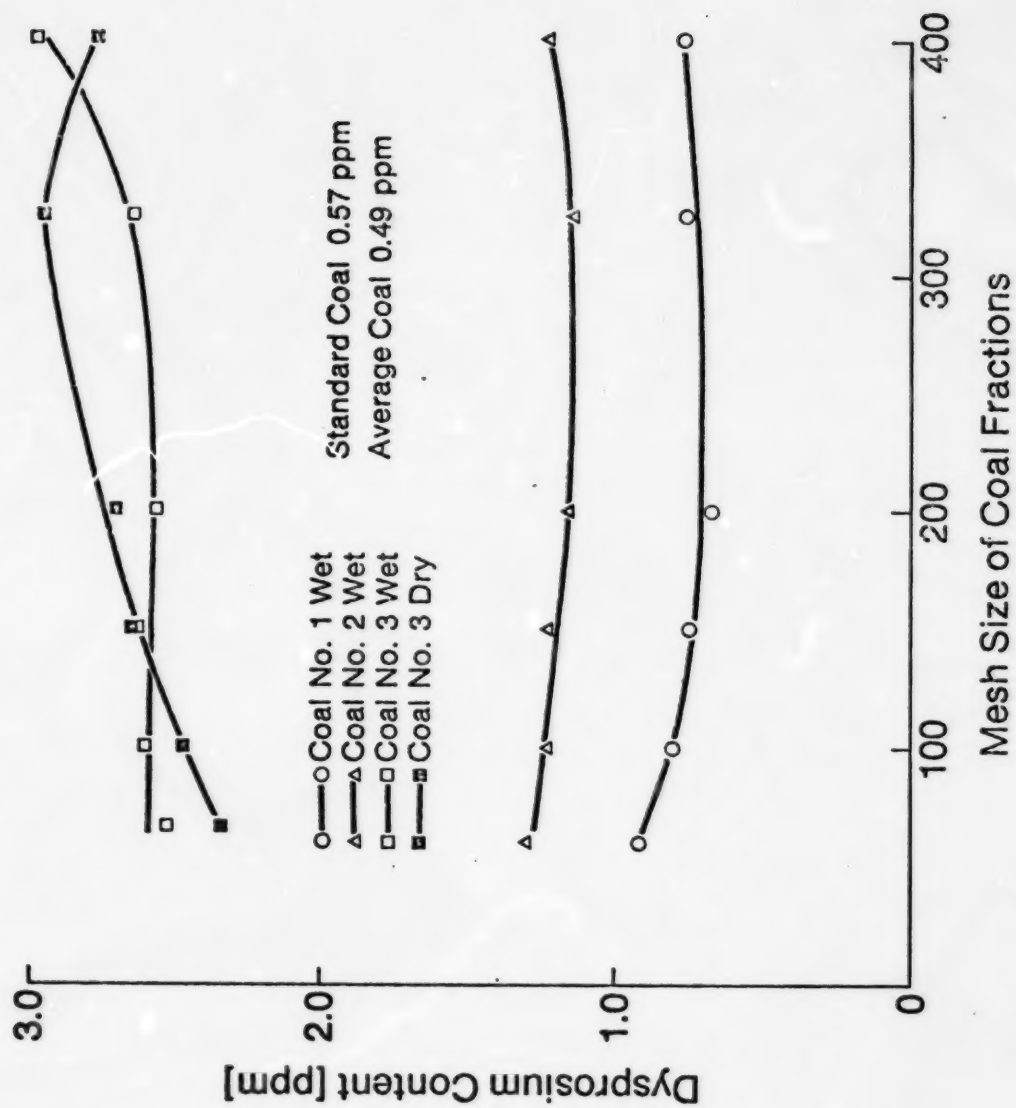


FIGURE 16. ALUMINUM CONTENT VERSUS MESH SIZE OF COAL FRACTIONS

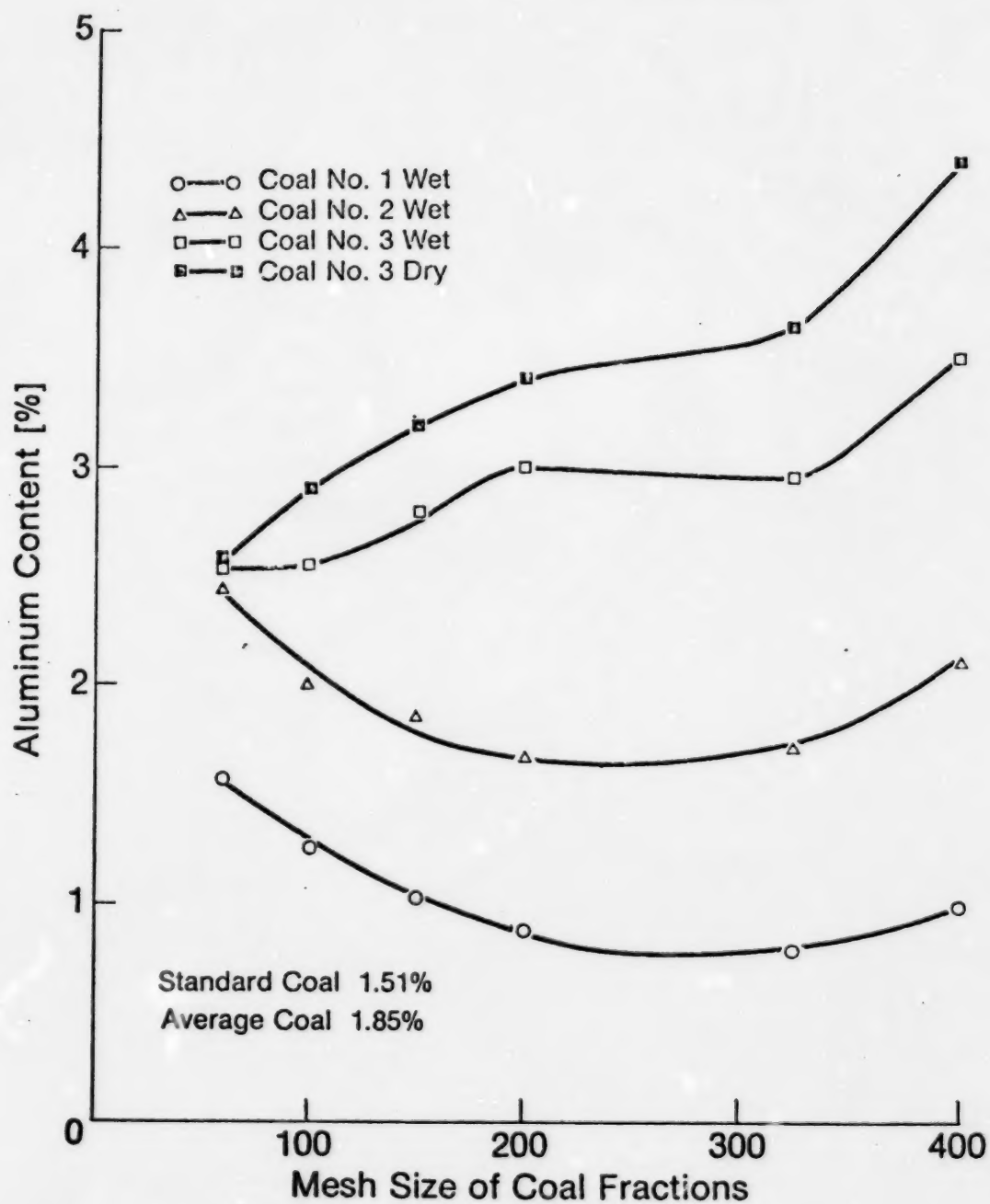


FIGURE 17. CALCIUM CONTENT VERSUS MESH SIZE OF COAL FRACTIONS

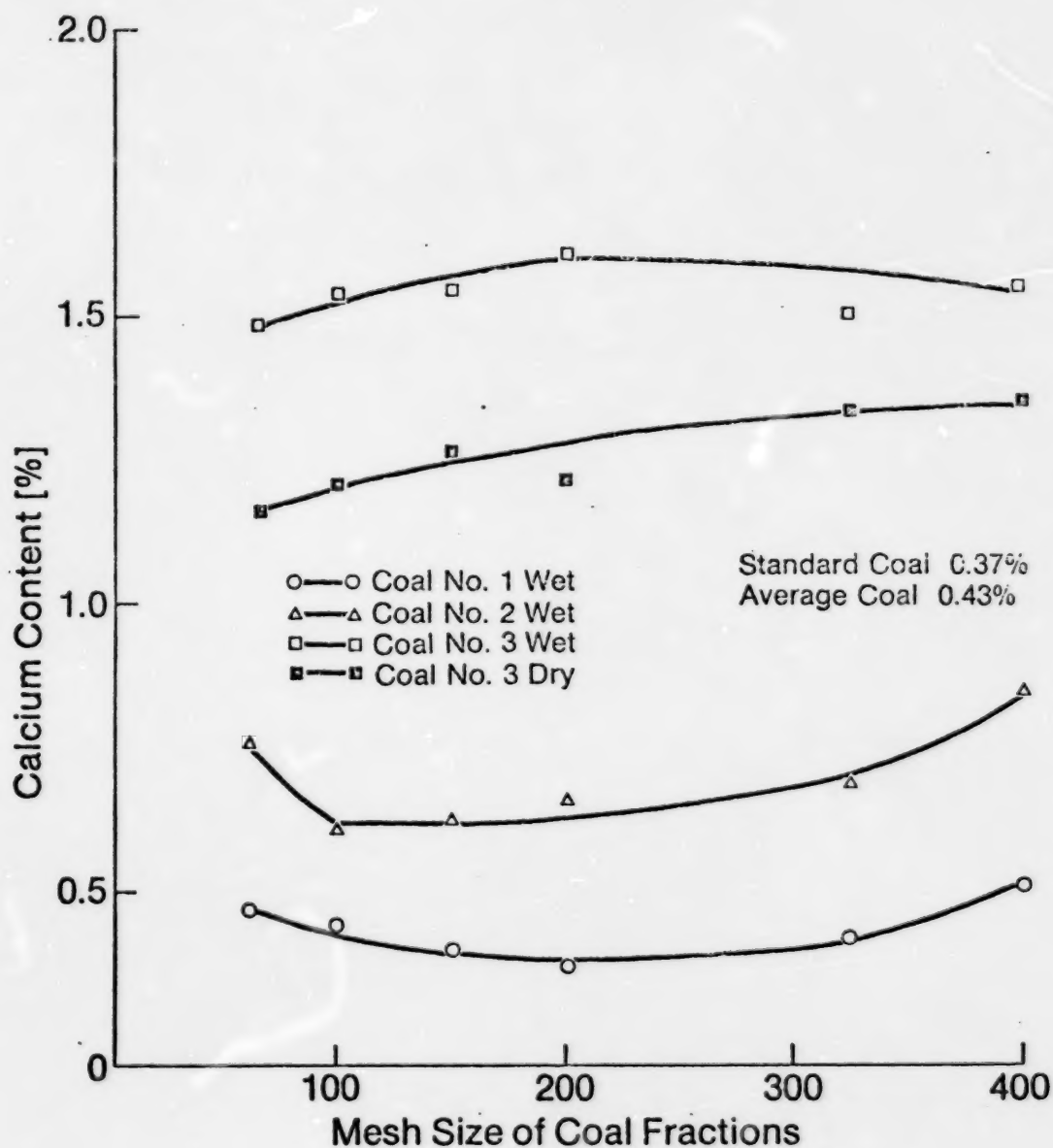


FIGURE 18. MAGNESIUM CONTENT VERSUS MESH SIZE OF COAL FRACTIONS

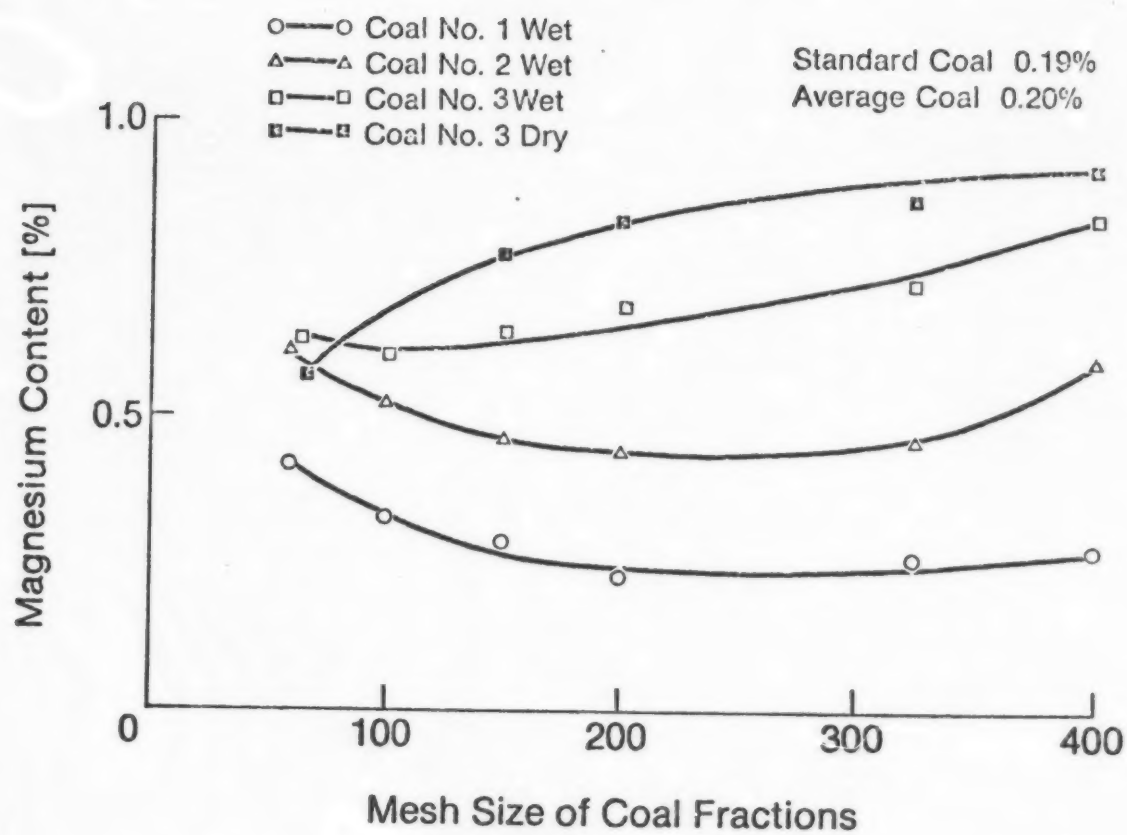


FIGURE 19. MANGANESE CONTENT VERSUS MESH SIZE OF COAL FRACTIONS

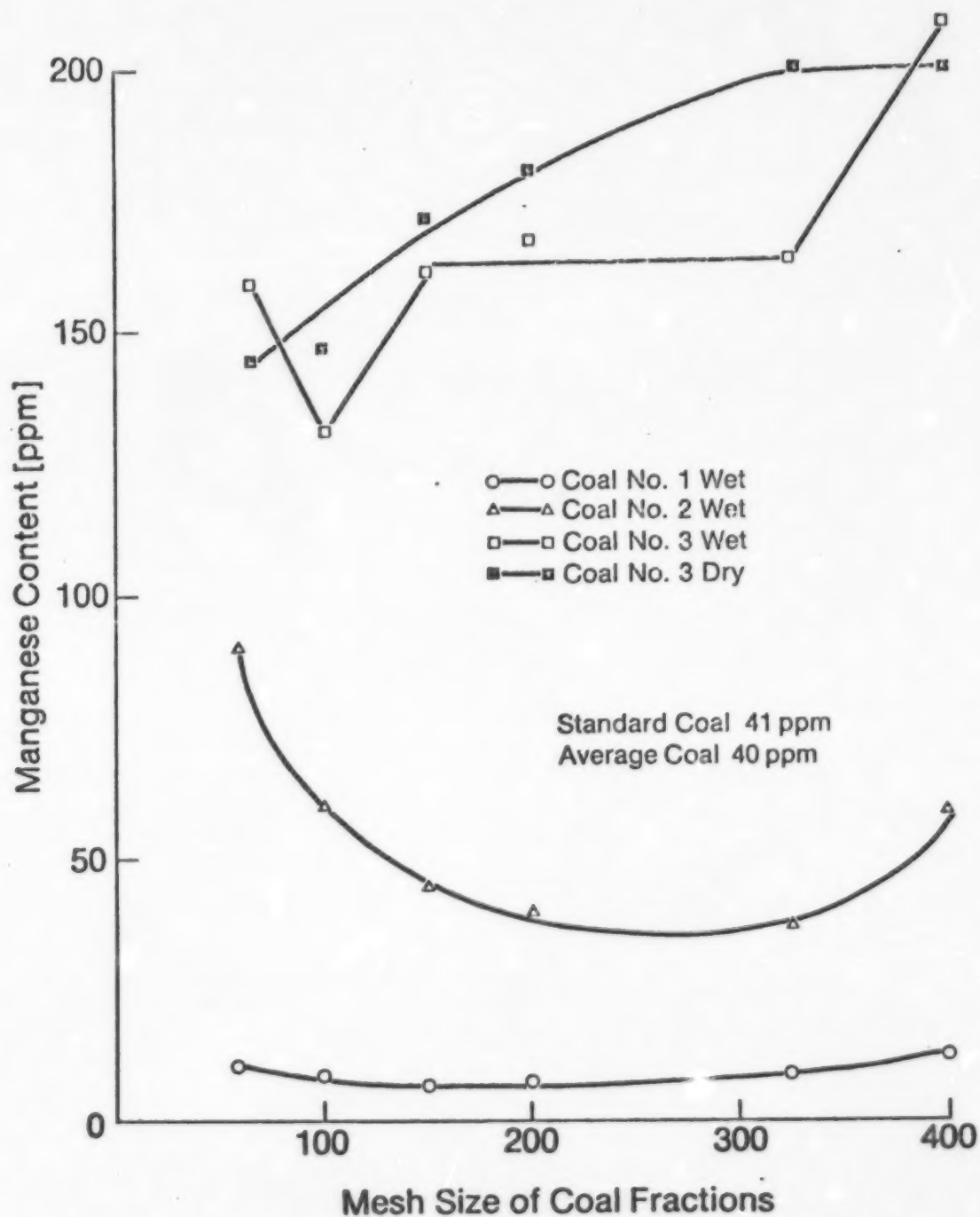


FIGURE 20. SODIUM CONTENT VERSUS MESH SIZE OF COAL FRACTIONS

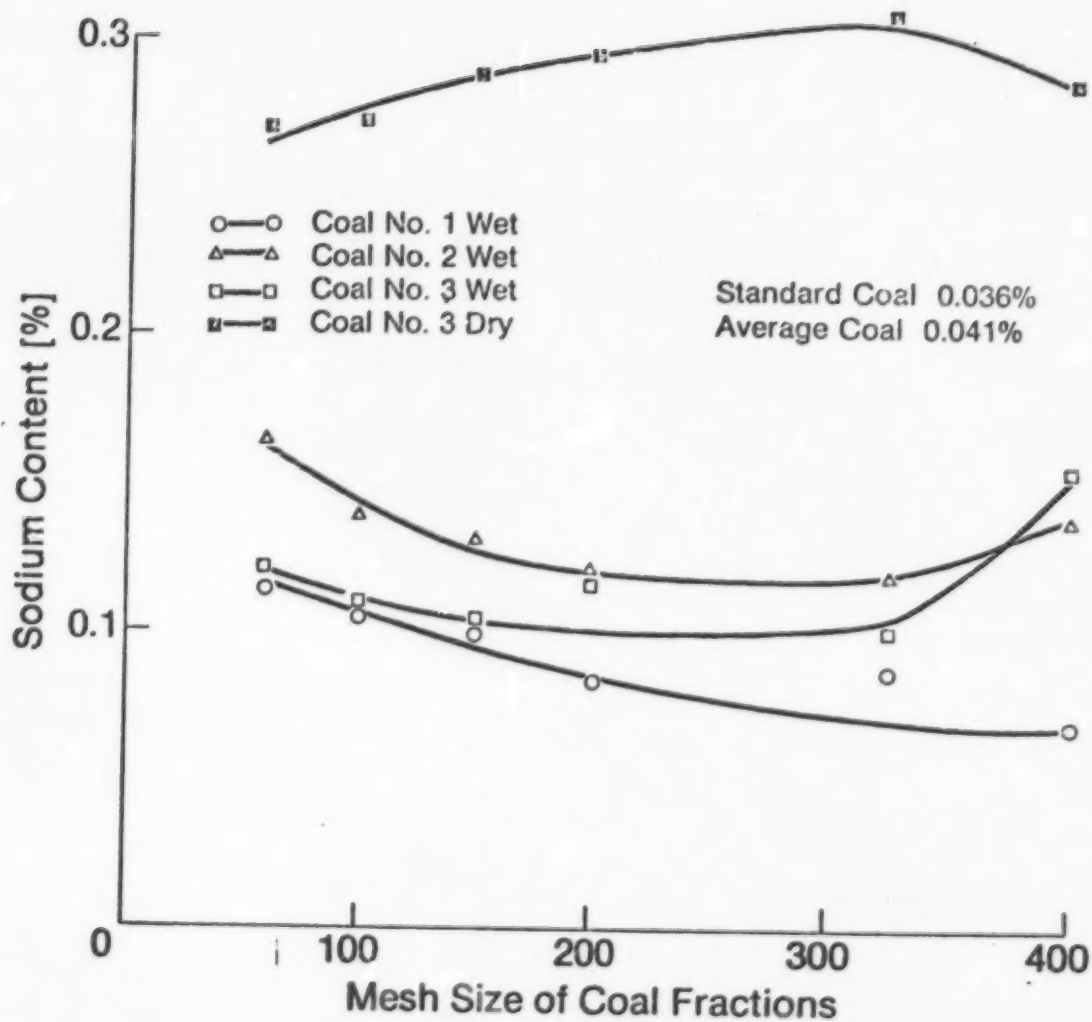


FIGURE 21. TITANIUM CONTENT VERSUS MESH SIZE OF COAL FRACTIONS

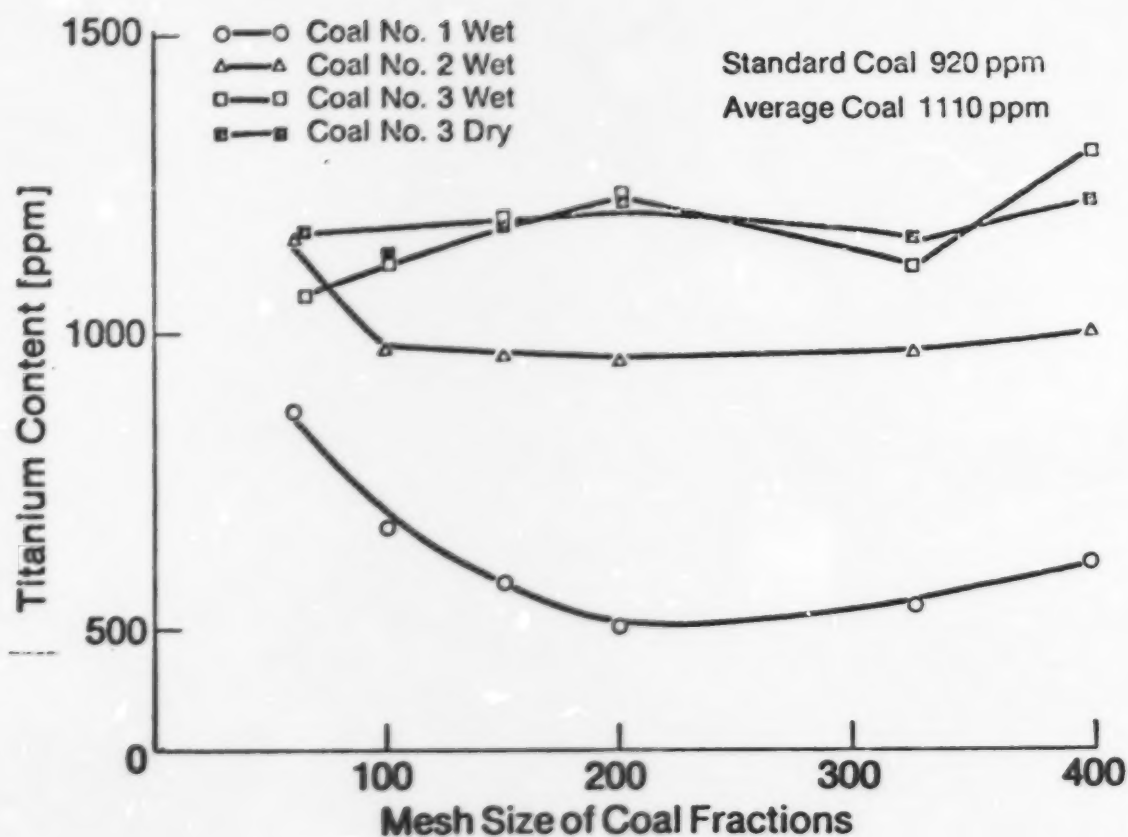


FIGURE 22. VANADIUM CONTENT VERSUS MESH SIZE OF COAL FRACTIONS

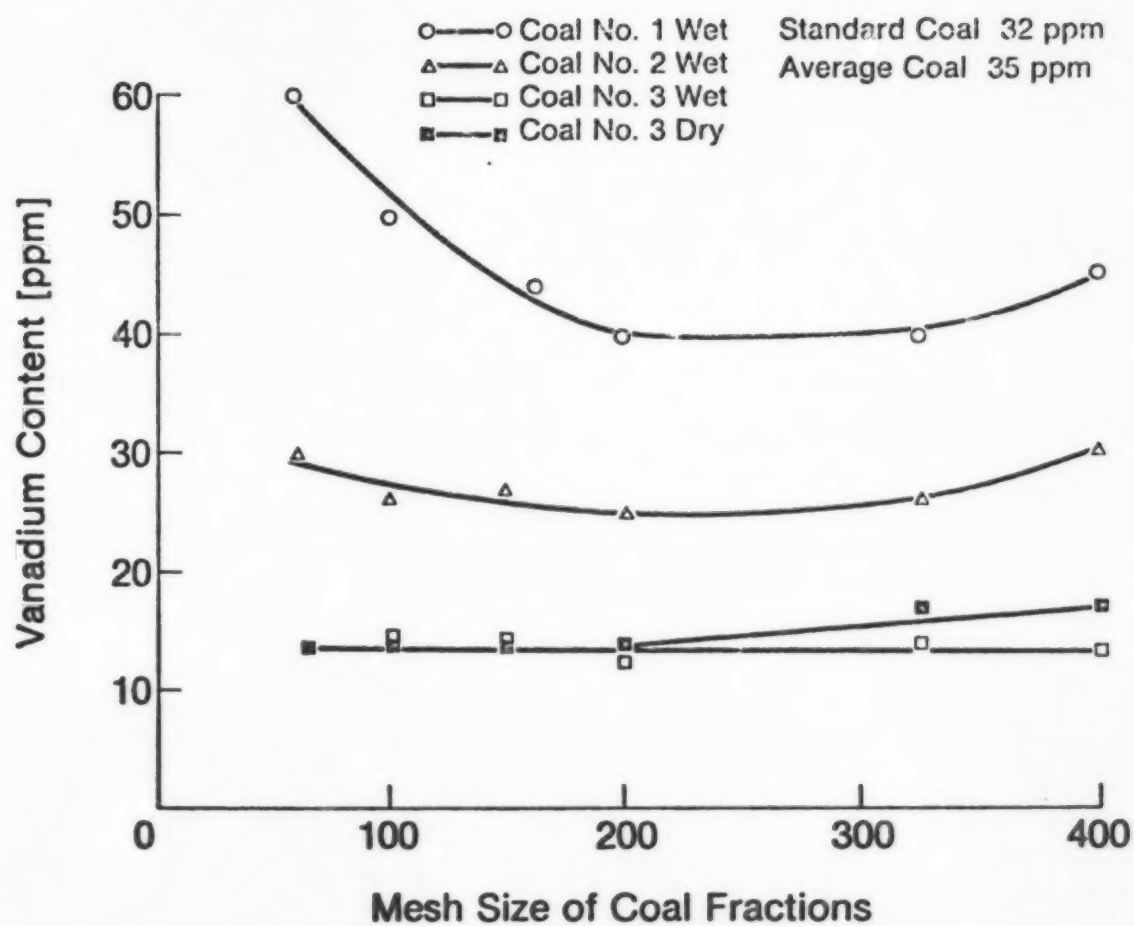


FIGURE 23. CHLORINE CONTENT VERSUS MESH SIZE OF COAL FRACTIONS

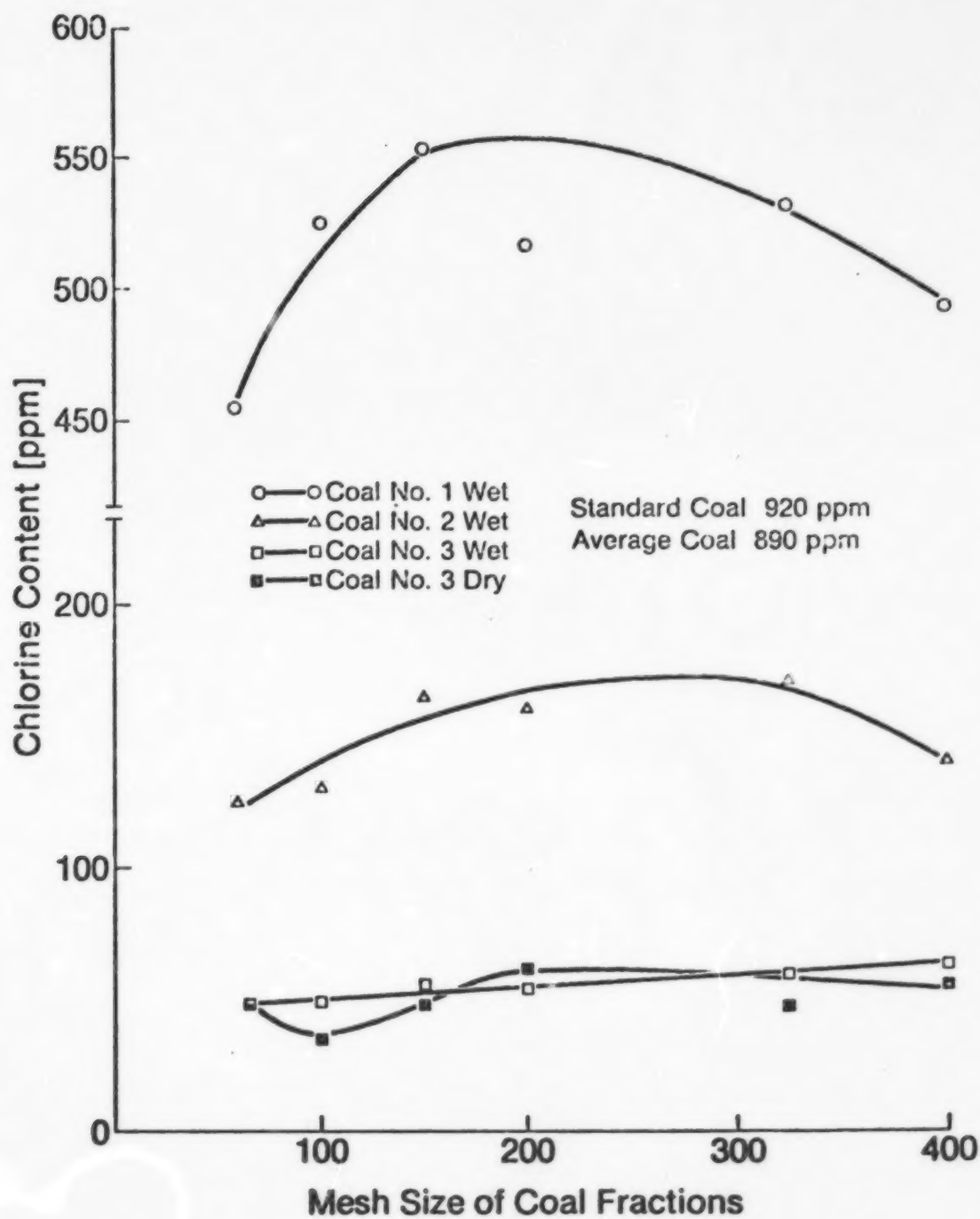


FIGURE 24. BARIUM CONTENT VERSUS MESH SIZE OF COAL FRACTIONS

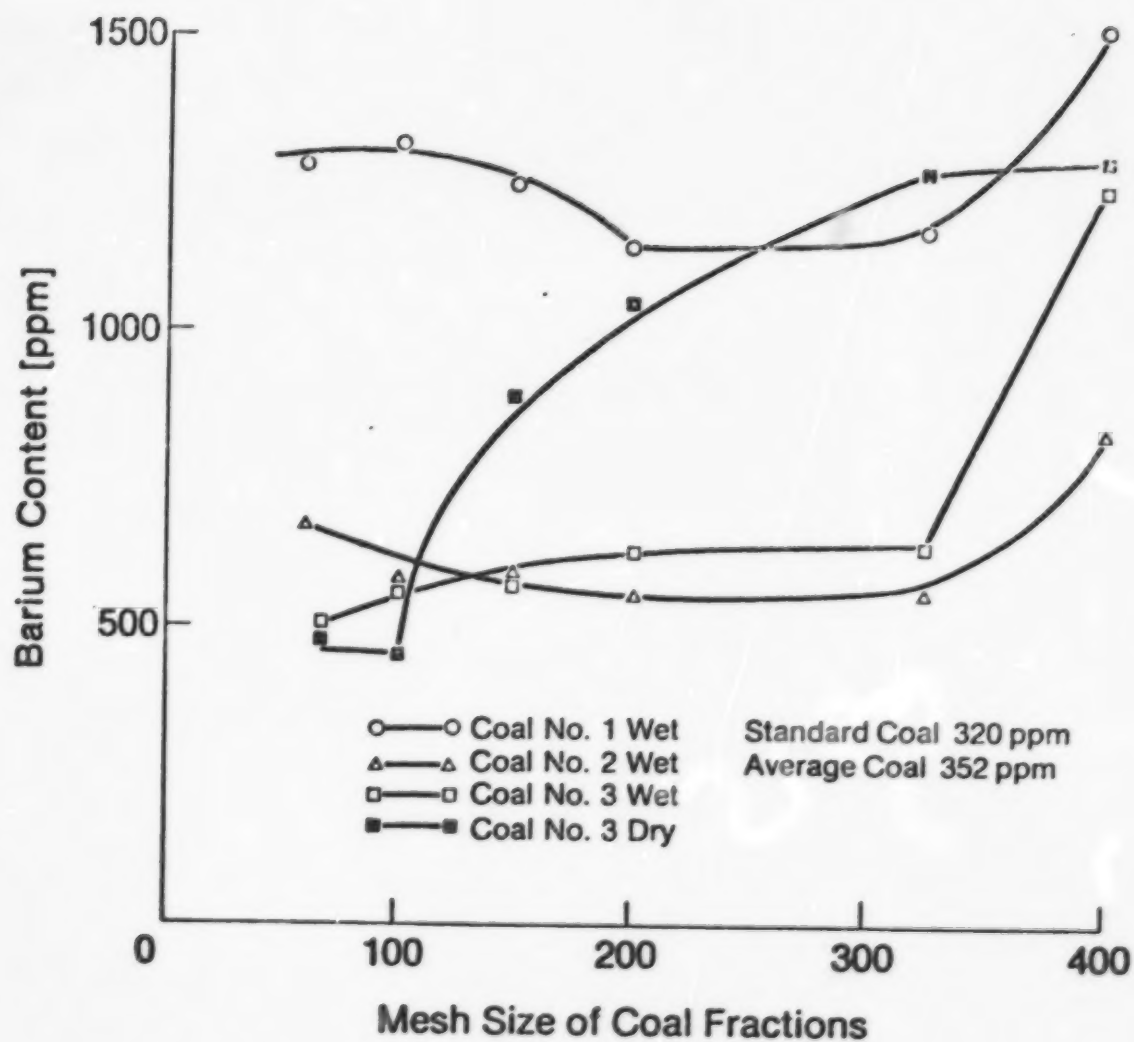


FIGURE 25. STRONTIUM CONTENT VERSUS MESH SIZE OF COAL FRACTIONS

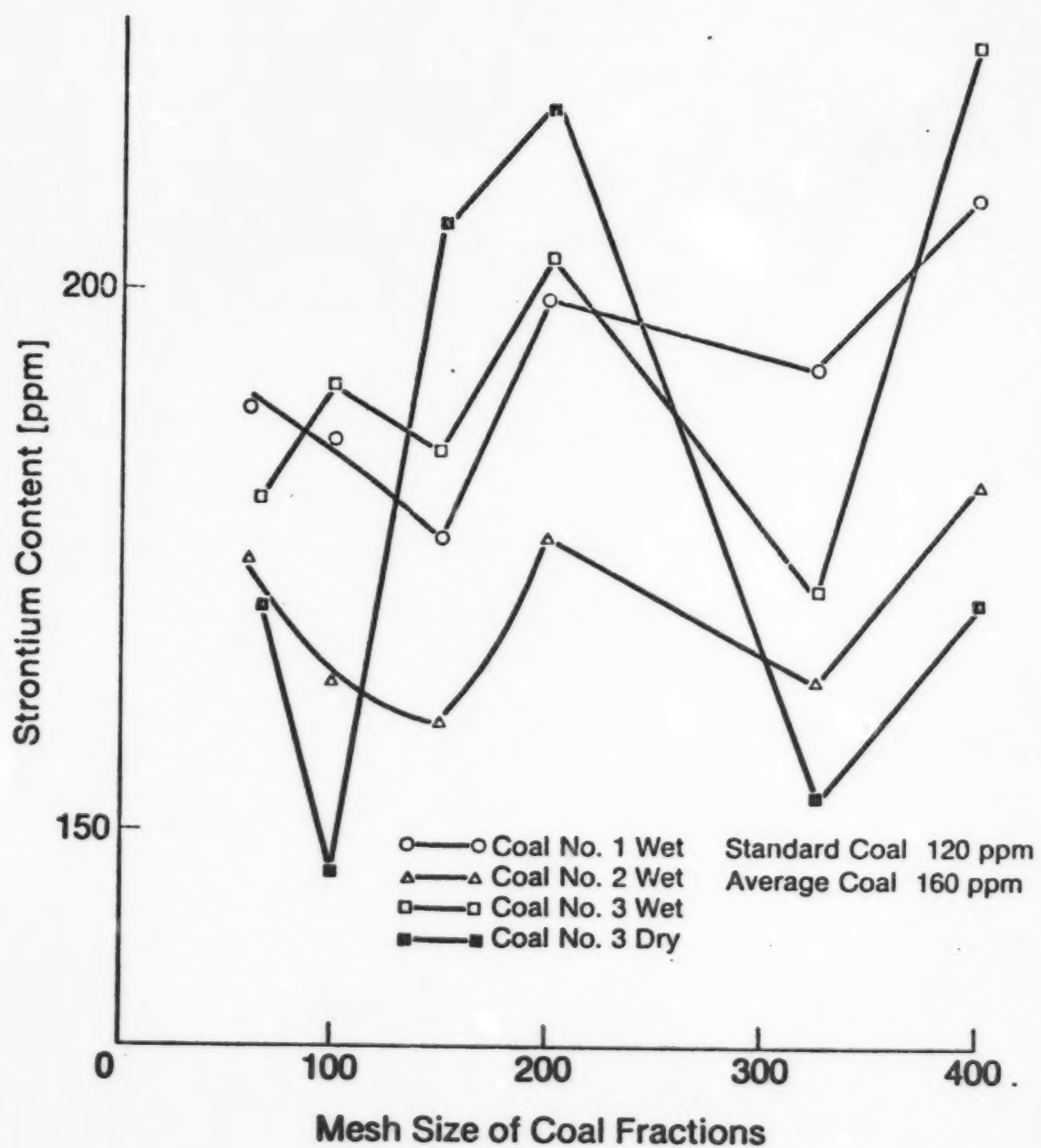


FIGURE 26. BROMINE CONTENT VERSUS MESH SIZE OF COAL FRACTIONS

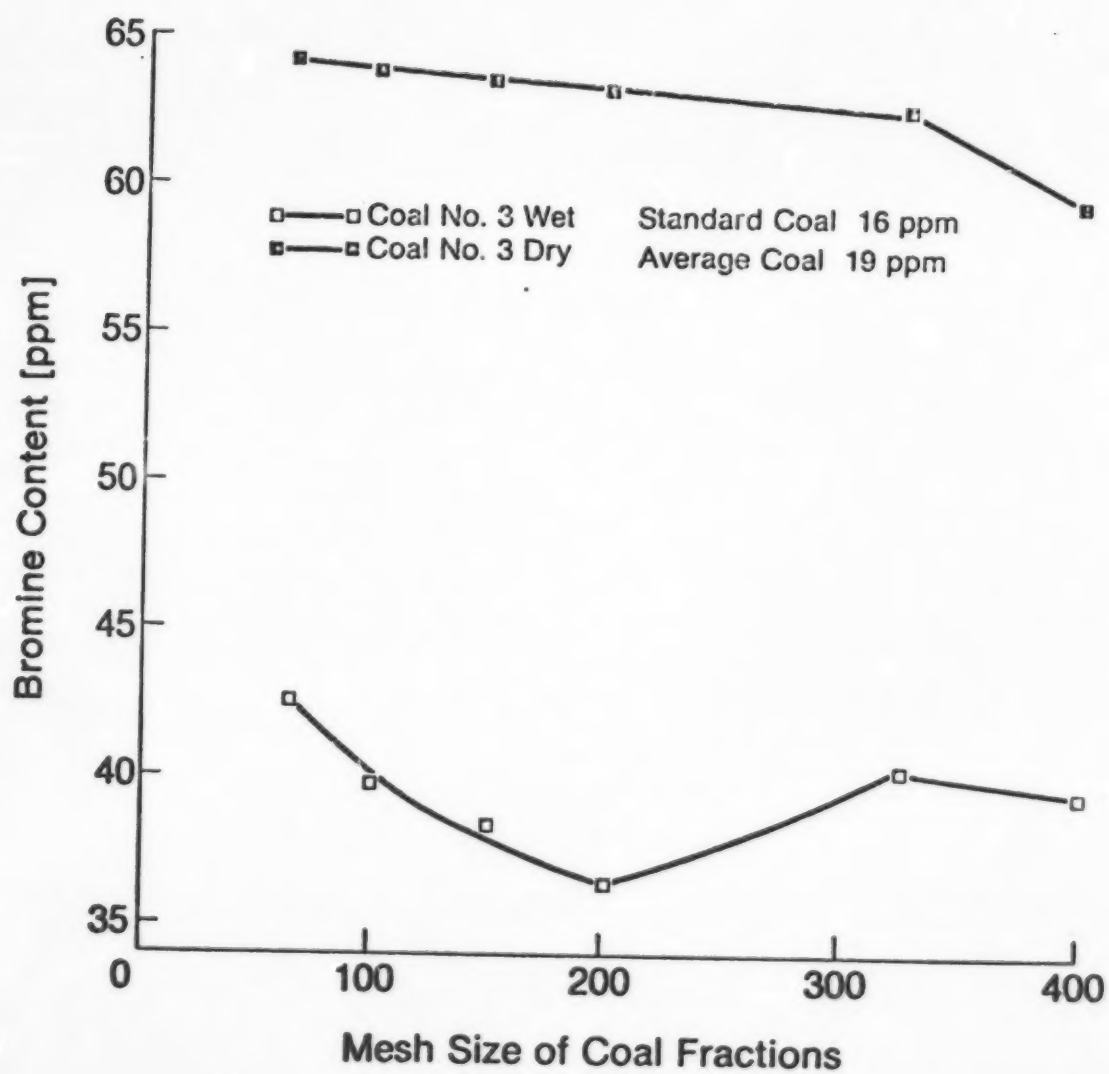


FIGURE 27 CRITICAL VELOCITY, V_C , VERSUS PARTICLE DIAMETER, D ,
FOR THYMOL - COAL SAMPLE No. 2

76.

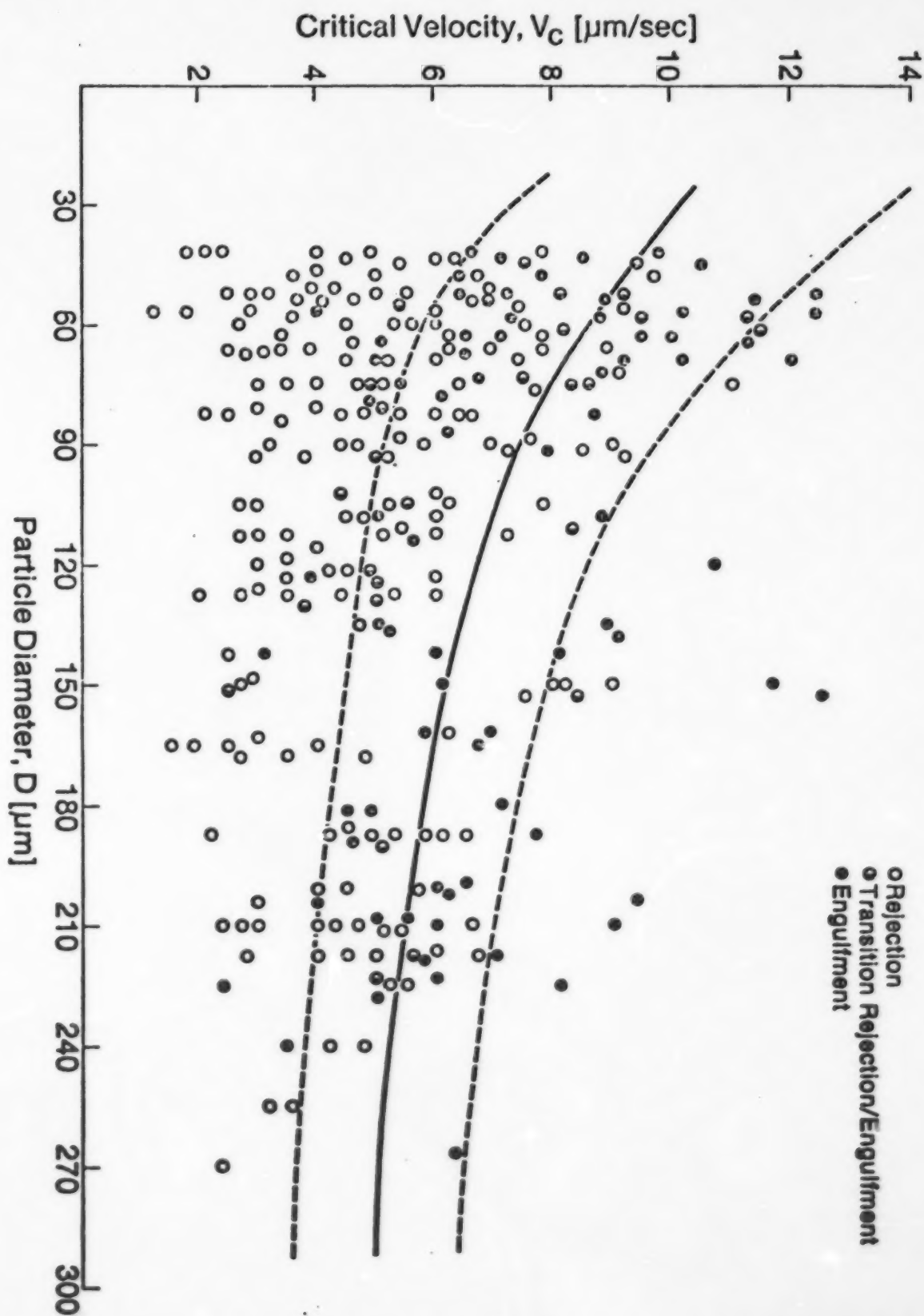


FIGURE 28 CRITICAL VELOCITY, V_c , VERSUS PARTICLE DIAMETER, D ,
FOR BIPHENYL - COAL SAMPLE No. 2

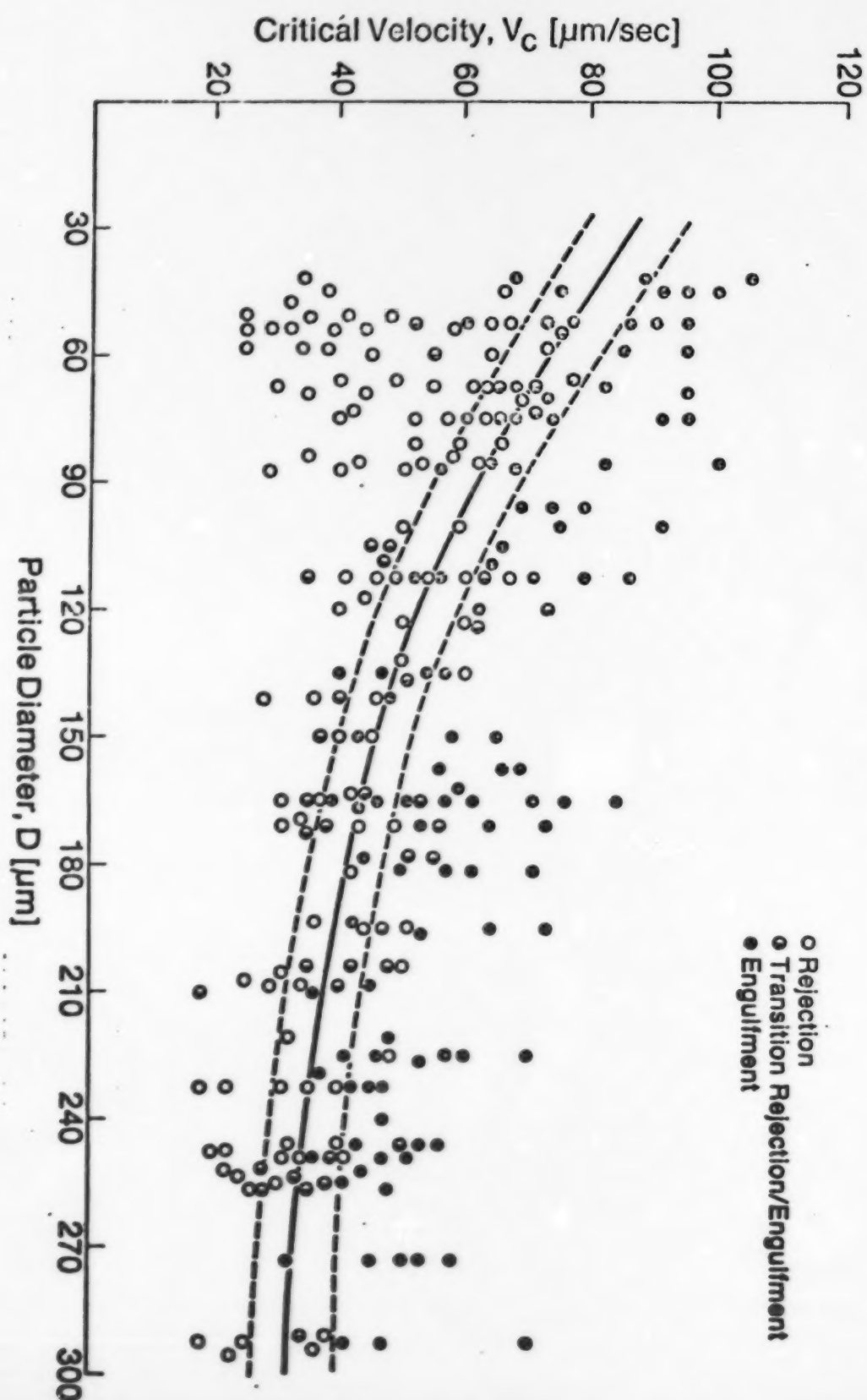


FIGURE 29 CRITICAL VELOCITY, V_C , VERSUS PARTICLE DIAMETER, D ,
FOR NAPHTHALENE - COAL SAMPLE No. 2

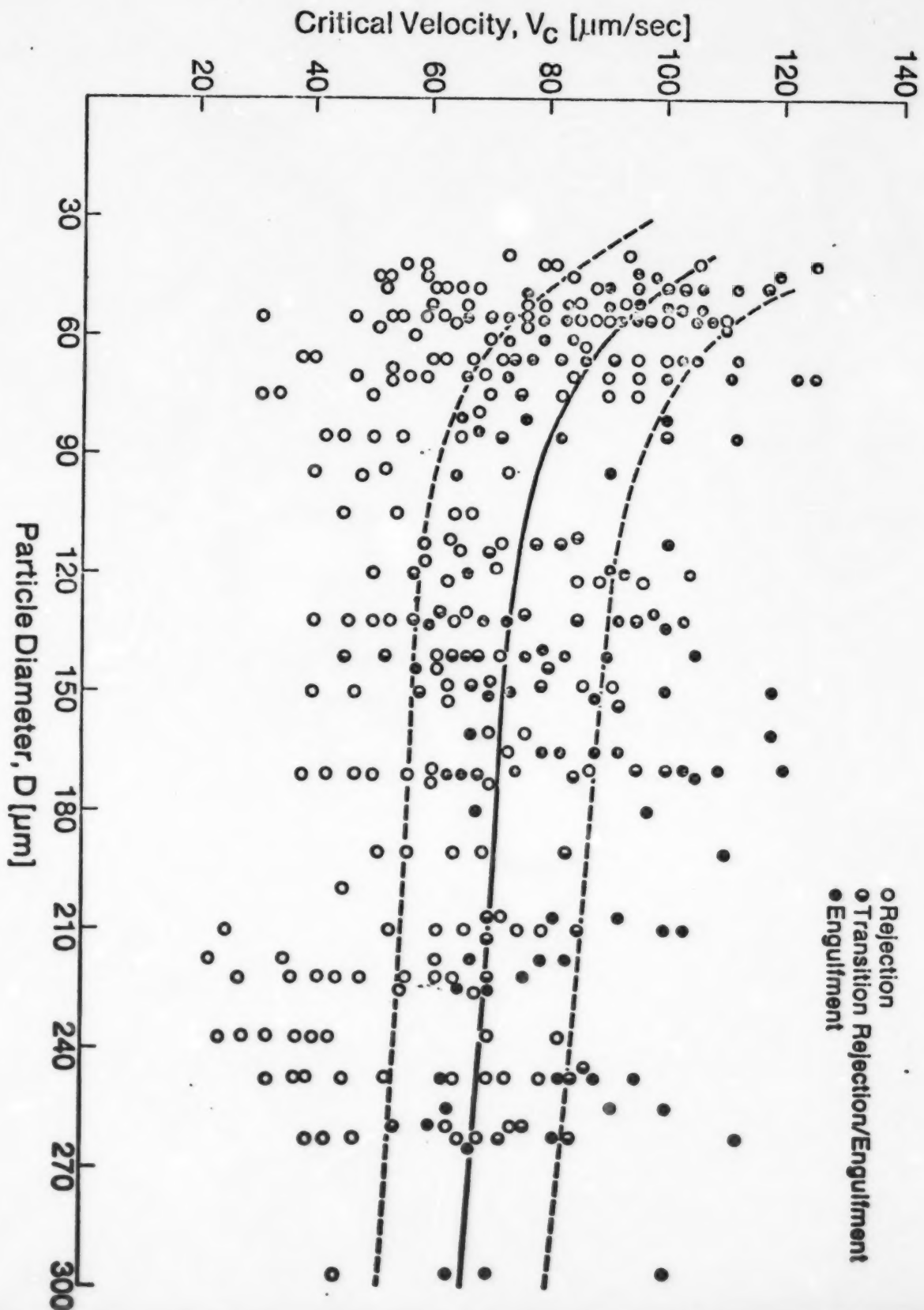
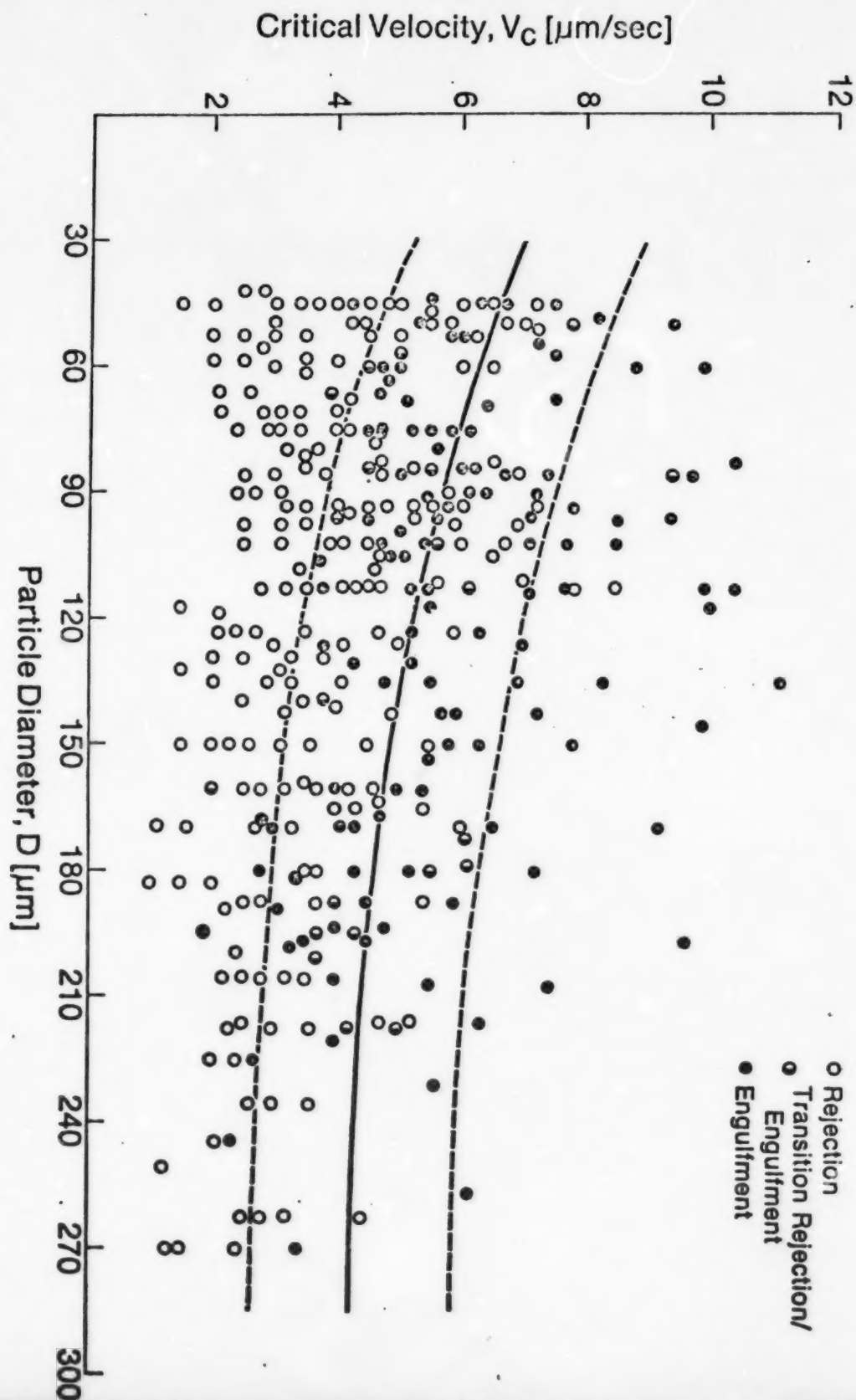


FIGURE 30 CRITICAL VELOCITY, V_C , VERSUS PARTICLE DIAMETER, D ,
FOR THYMOL - COAL SAMPLE NO. 3 WET



80.

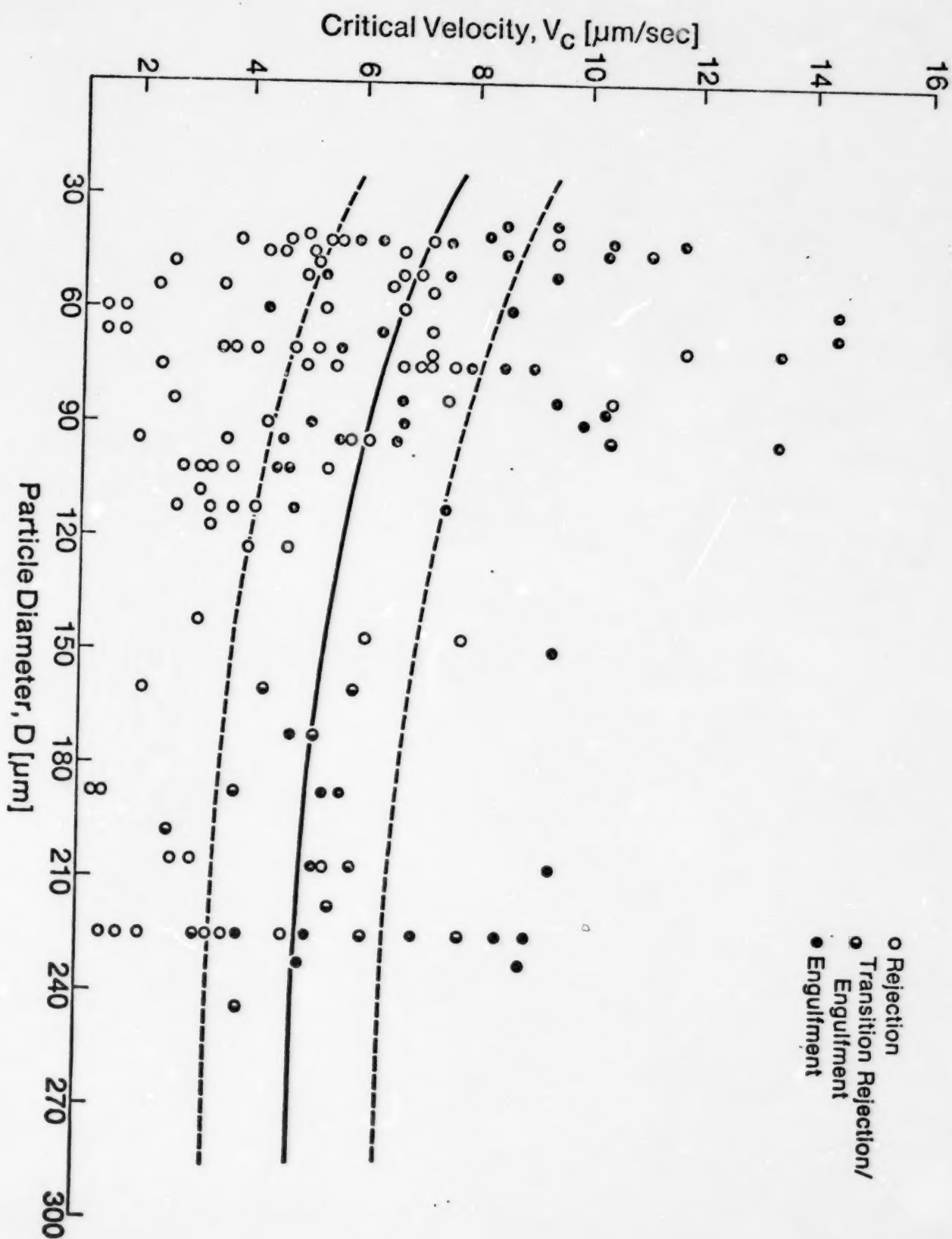
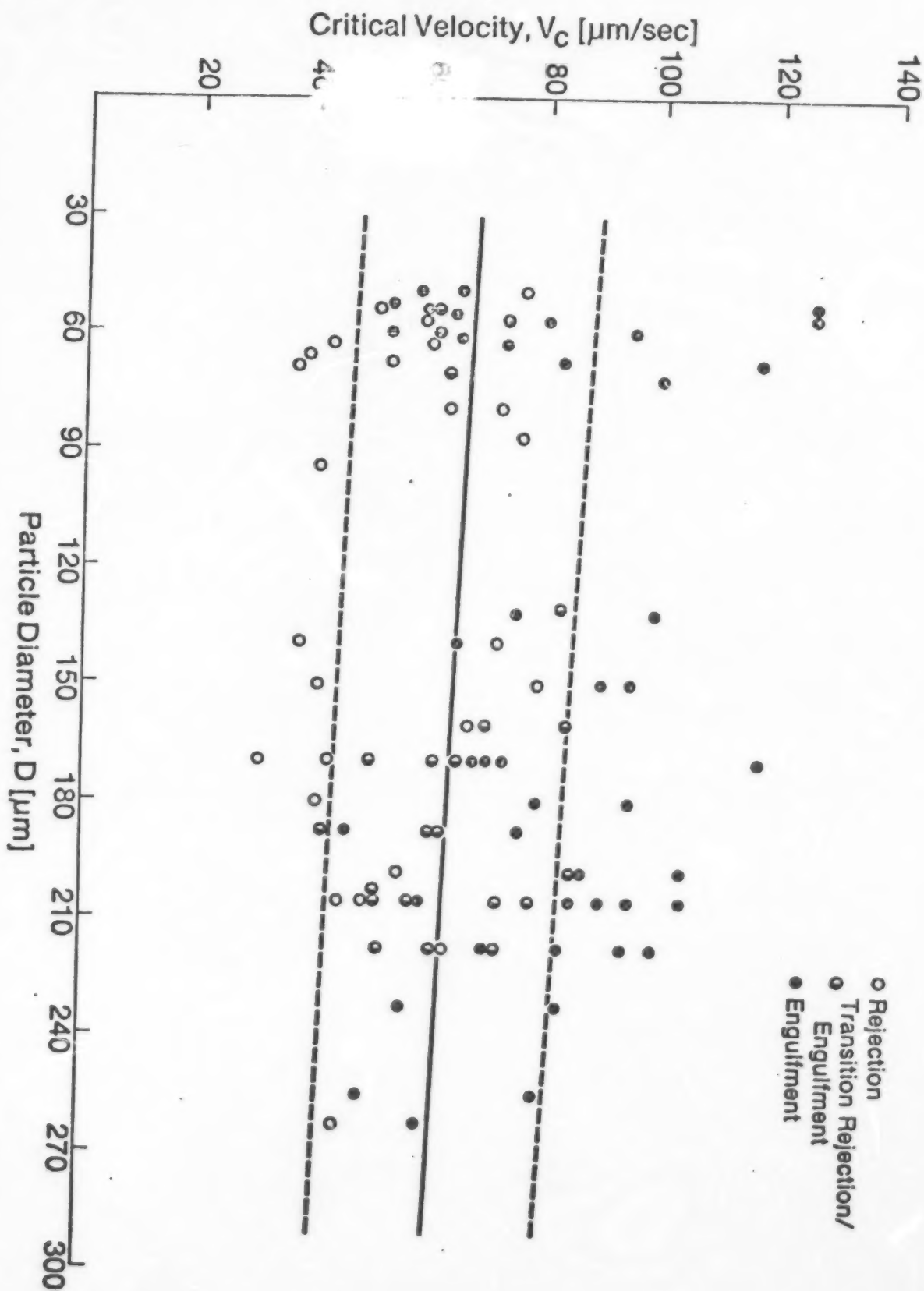


FIGURE 32 CRITICAL VELOCITY, V_c , VERSUS PARTICLE DIAMETER, D , 81.
FOR BIPHENYL - COAL SAMPLE NO. 3 WET



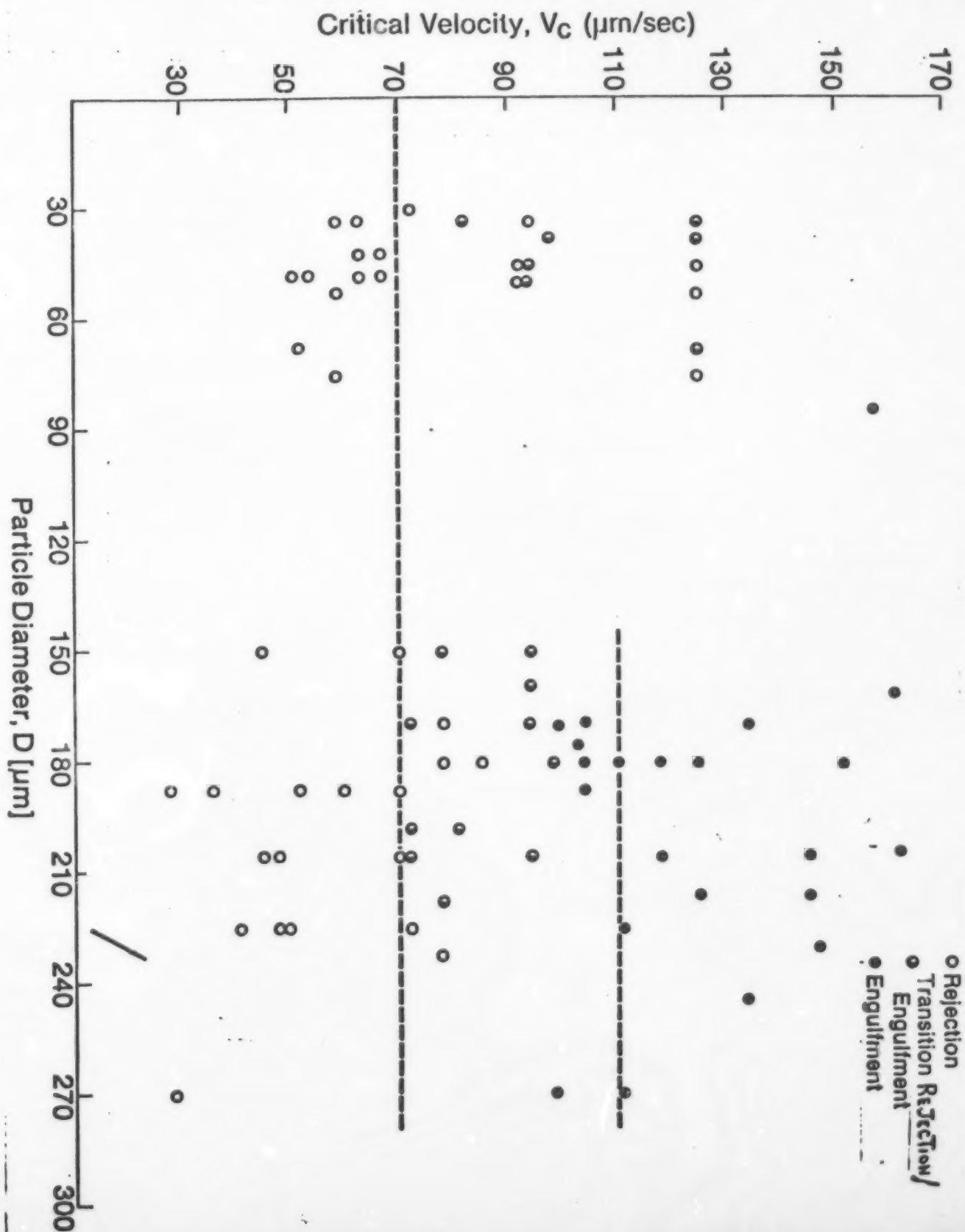


FIGURE 34 SURFACE TENSION, γ_{pv} , OF COAL SAMPLE No. 2 AS A FUNCTION OF PARTICLE DIAMETER, D , DETERMINED FROM THYMOL

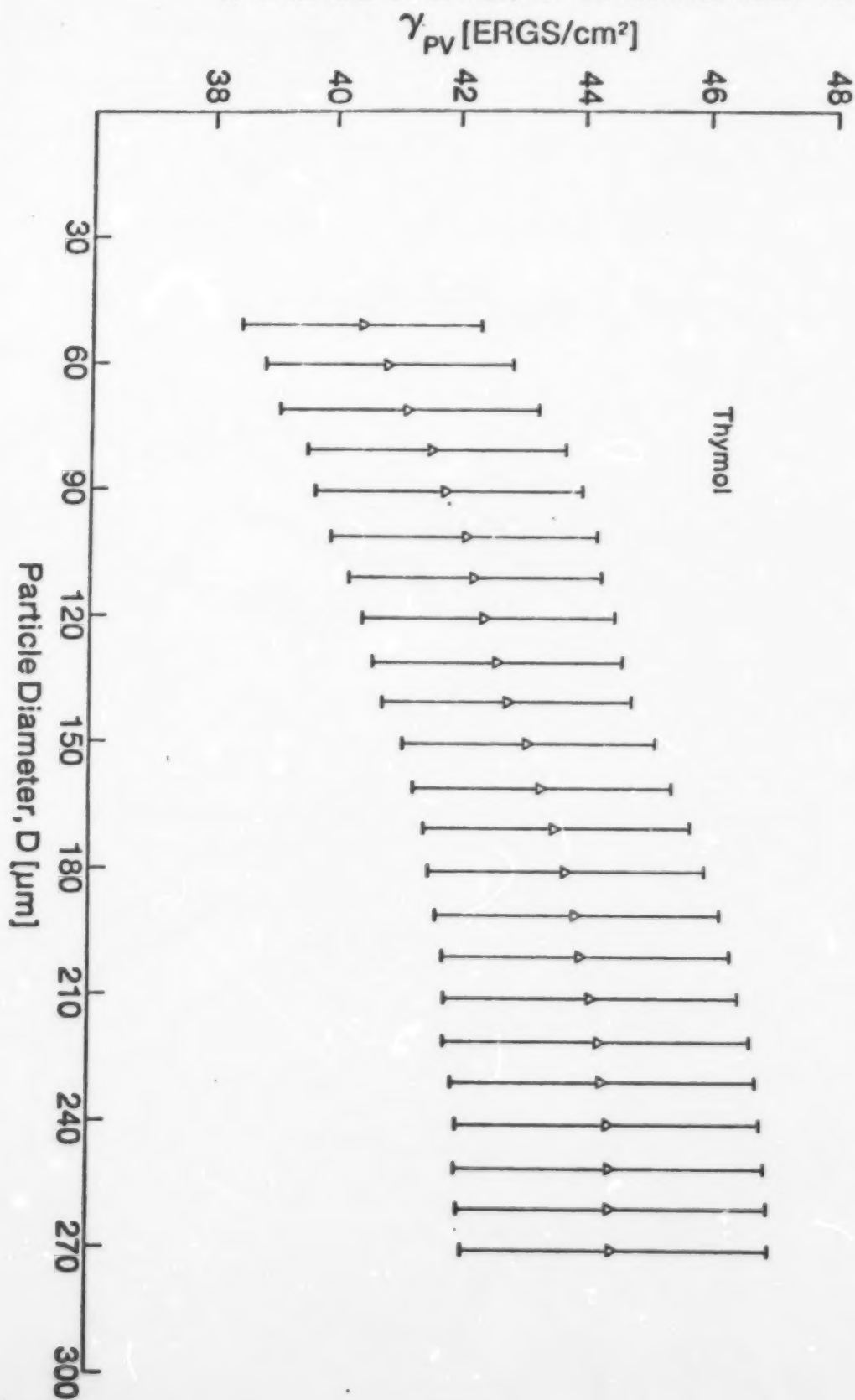


FIGURE 35 SURFACE TENSION, γ_{py} , OF COAL SAMPLE No. 2 AS A FUNCTION OF PARTICLE DIAMETER, D , DETERMINED FROM BIPHENYL

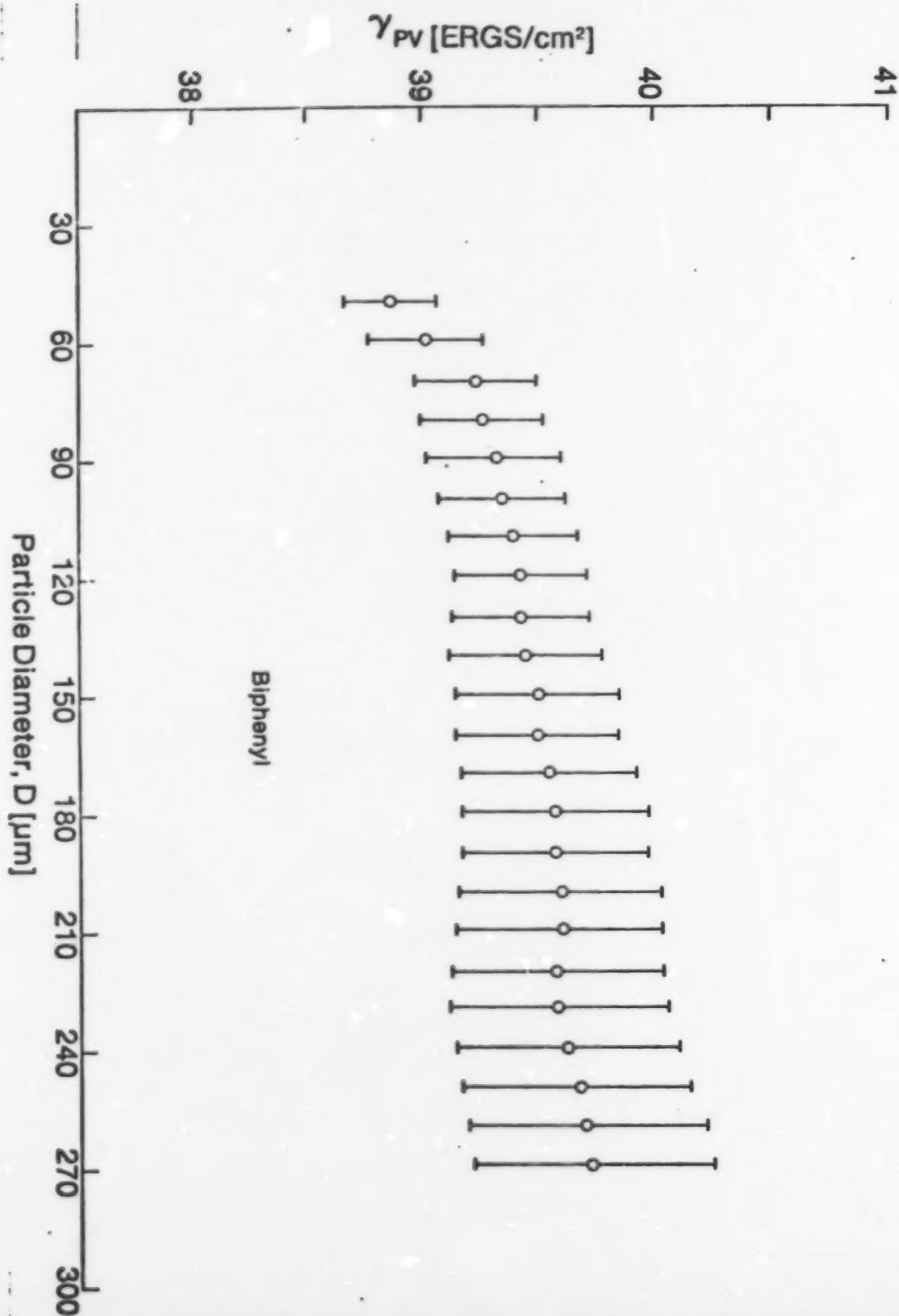


FIGURE 36 SURFACE TENSION, γ_{pv} , OF COAL SAMPLE No. 2 AS A FUNCTION OF PARTICLE DIAMETER, D , DETERMINED FROM NAPHTHALENE

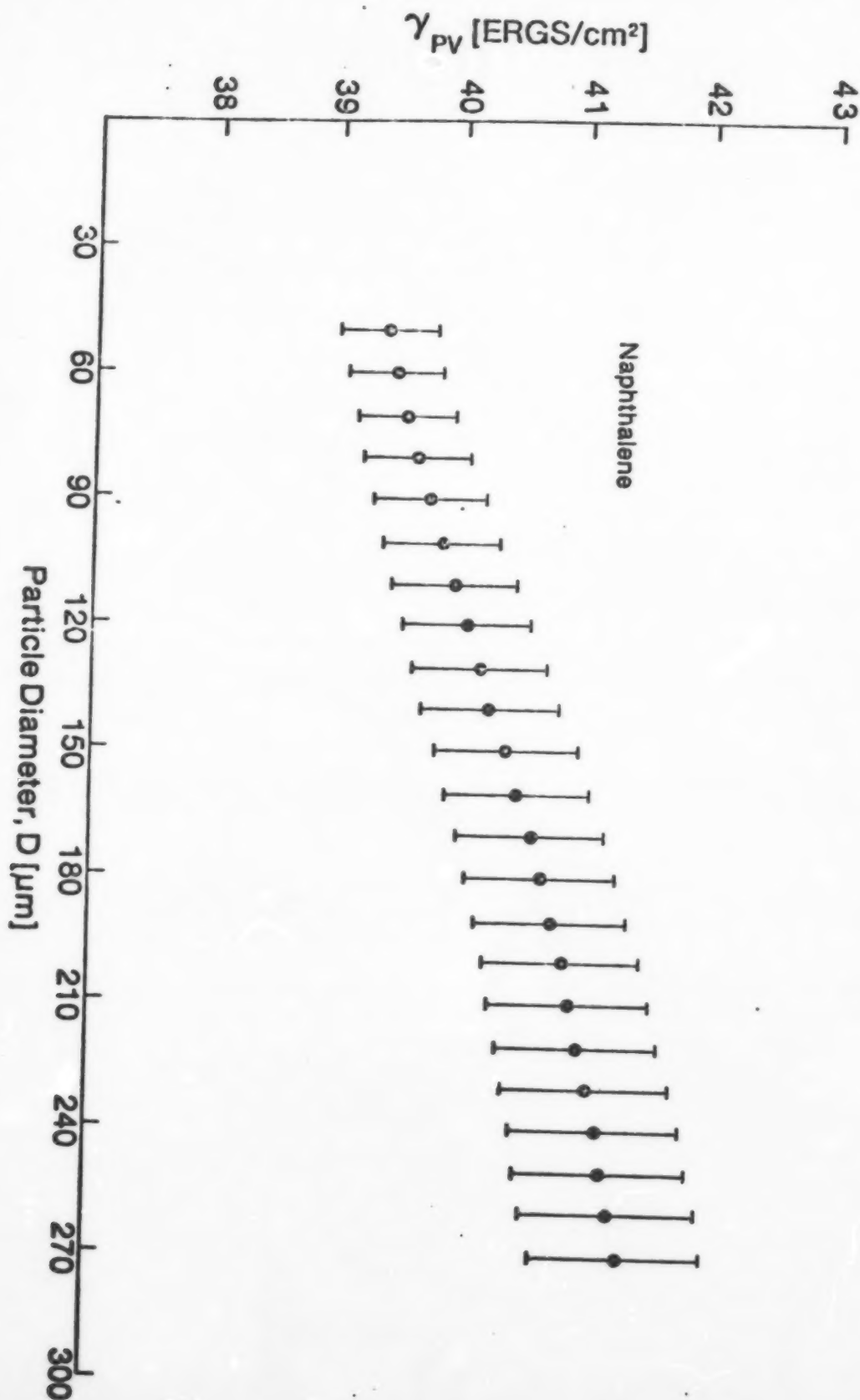


FIGURE 37 CONTACT ANGLE, θ , OF WATER ON COAL SAMPLE No. 2 AS A FUNCTION OF PARTICLE DIAMETER, D , DETERMINED FROM THYMOL

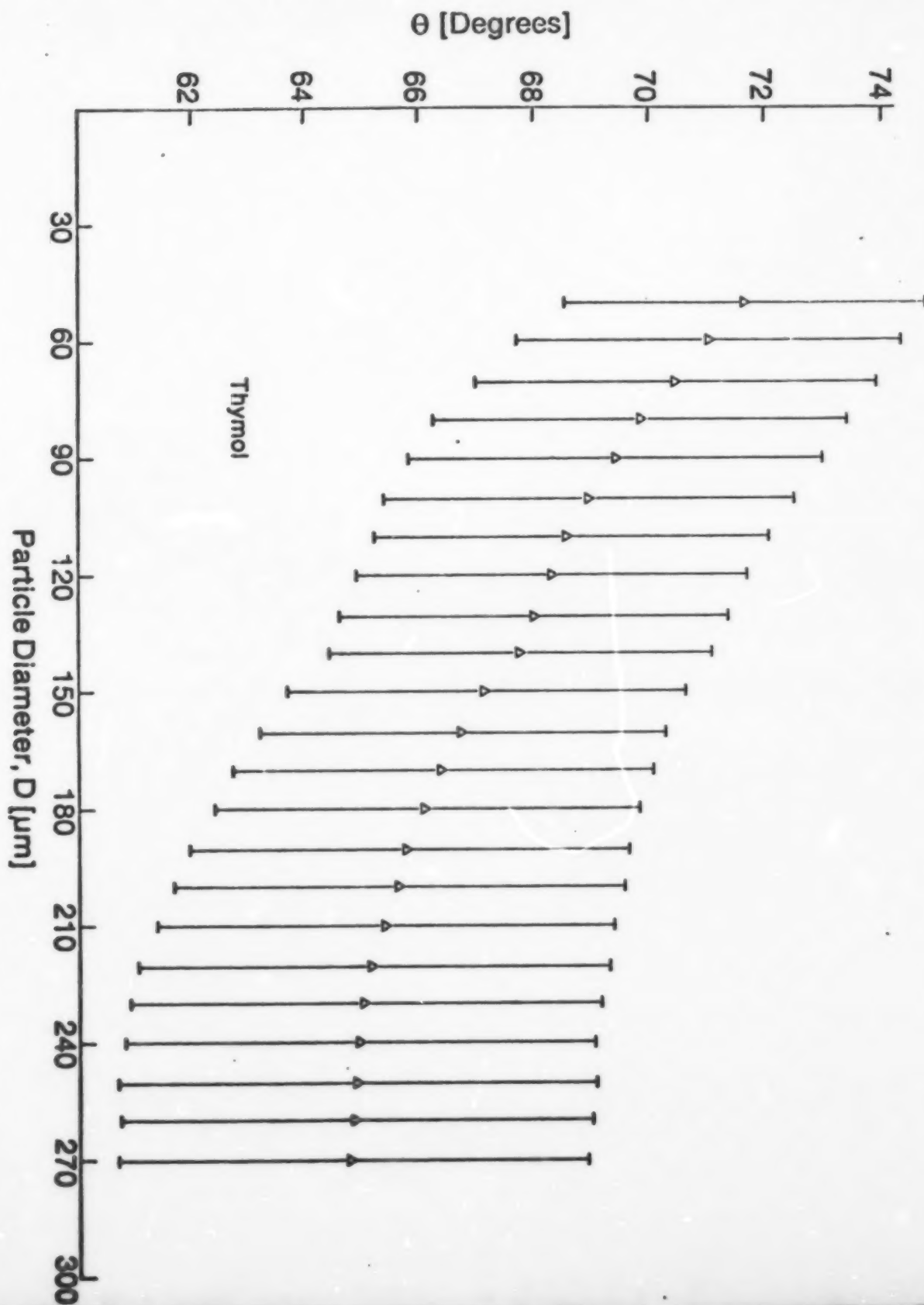


FIGURE 38 CONTACT ANGLE, θ , OF WATER ON COAL SAMPLE No. 2 AS A FUNCTION OF PARTICLE DIAMETER, D , DETERMINED FROM BIPHENYL

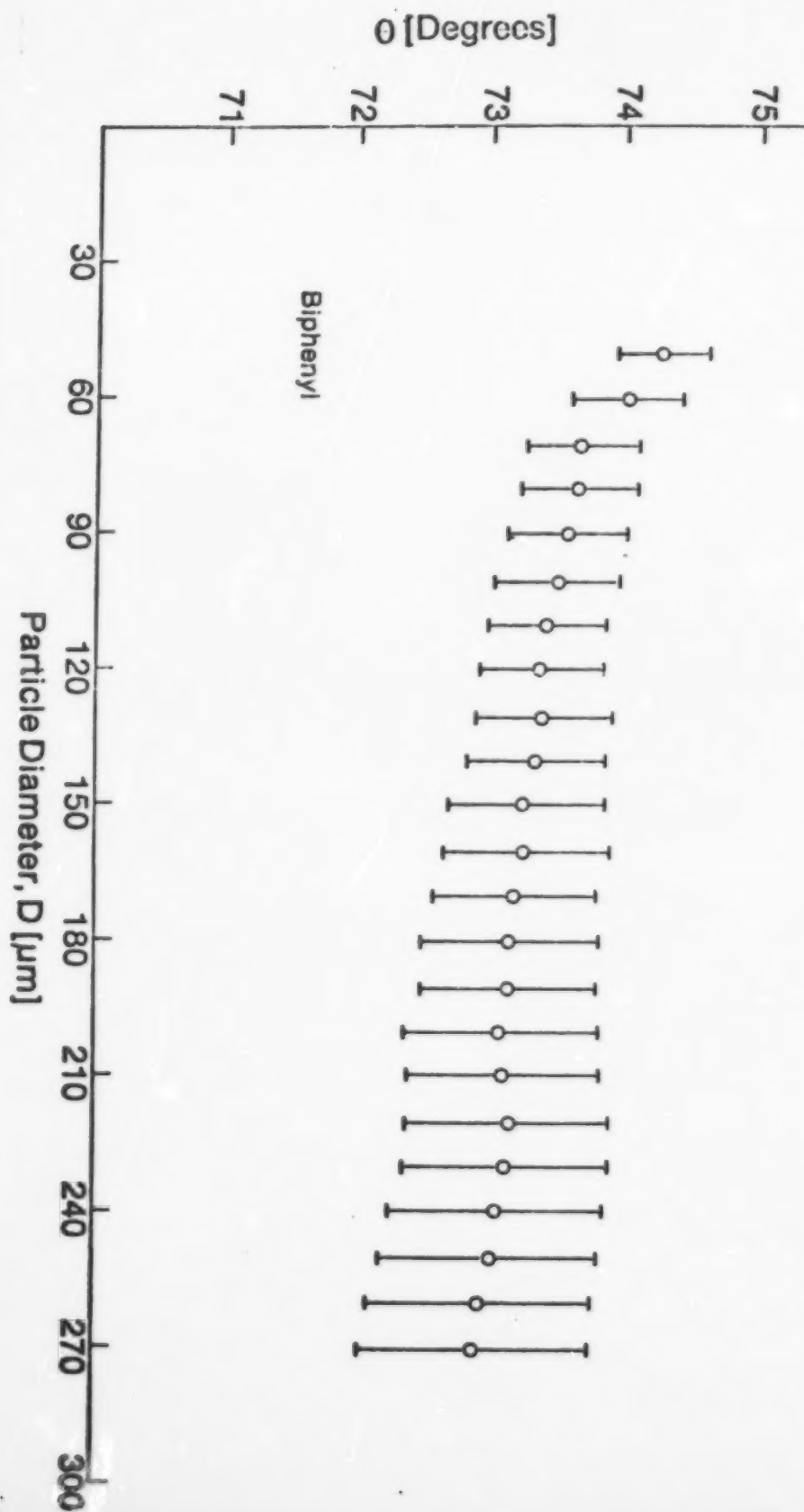


FIGURE 39 CONTACT ANGLE, θ , OF WATER ON COAL SAMPLE No. 2 AS A FUNCTION OF PARTICLE DIAMETER, D , DETERMINED FROM NAPHTHALENE

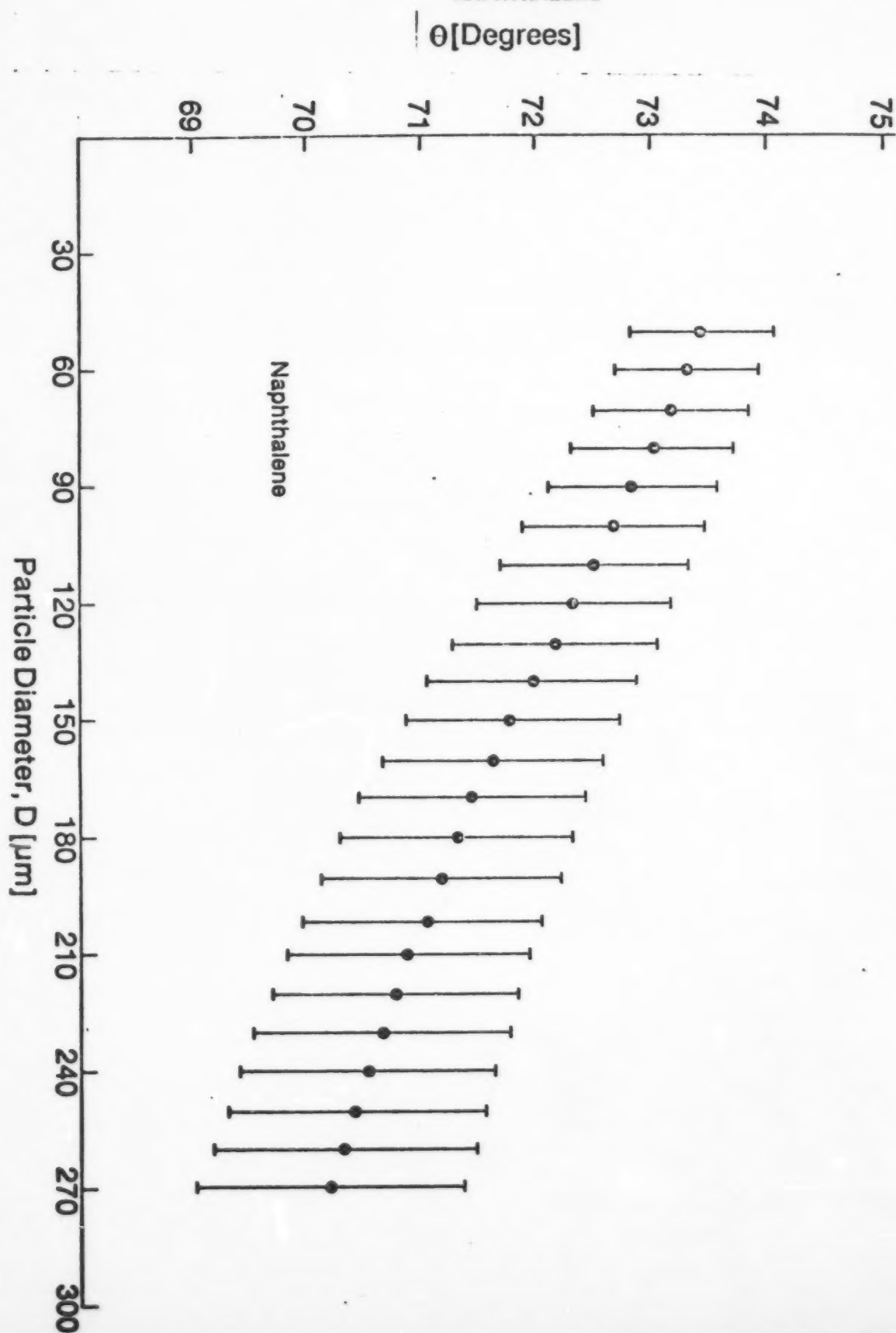


FIGURE 40 SURFACE TENSION, γ_{PV} , OF COAL SAMPLE No. 2 AS A FUNCTION OF PARTICLE DIAMETER, D ,

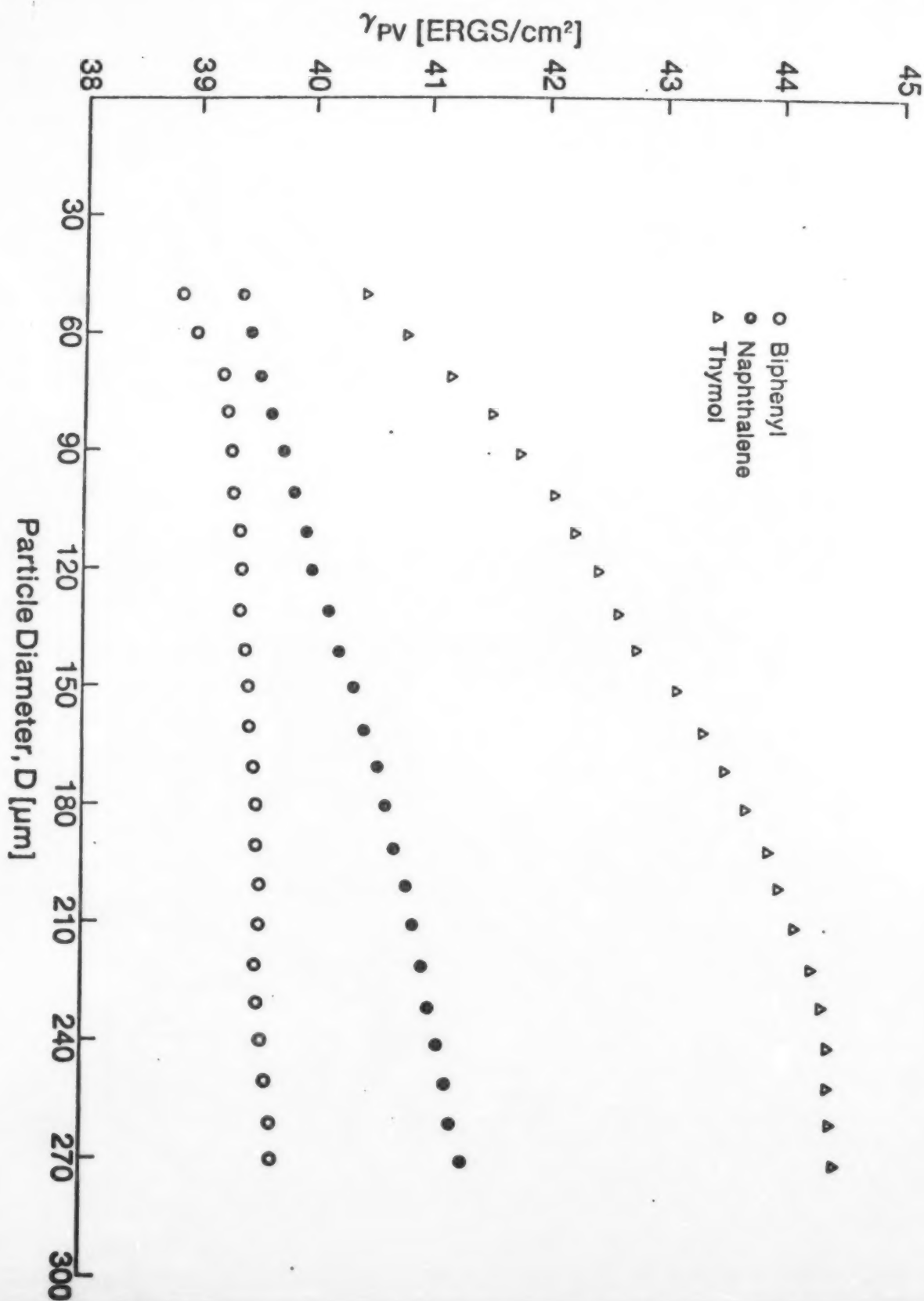


FIGURE 41 CONTACT ANGLE, θ , OF WATER ON COAL SAMPLE No. 2 AS A FUNCTION OF PARTICLE DIAMETER, D .

